

Use of Degraded Water Sources as Cooling Water in Power Plants

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Use of Degraded Water Sources as Cooling Water in Power Plants

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PRODUCT DESCRIPTION

In electricity production, nearly all thermal power plants reject heat either to a large body of water (once-through cooling) or to the atmosphere via wet cooling towers—the predominant form of cooling in California. These towers, however, use considerable quantities of water. Competing state demands for freshwater have forced California thermal power plants to consider alternative cooling water supplies, though the availability of such supplies and data on their use and impact is limited. In fact, other than treated municipal effluent, few (if any) alternative sources of degraded water have been developed for cooling needs. EPRI and the California Energy Commission (CEC) cosponsored this project to provide basic tools and guidelines to public and private parties involved in source water evaluations for California power projects.

Results & Findings

Alternative water supplies—involving use of degraded or nonpotable water—offer significant opportunities for power plants to limit their use of freshwater. Potential sources of degraded water include contaminated groundwater, treated municipal effluent, industrial process water or wastewater, irrigation return water, brackish water, and other types of water impacted by humans or naturally-occurring minerals. This report investigates technological and environmental issues associated with the use of degraded water for cooling, by focusing on the following key areas:

Water quality requirements—This discussion of water quality criteria includes a six-step framework for evaluating source water chemistry, chemical criteria for cooling towers, cooling system design and operating impacts, source water screening, treatment requirements, and disposal issues. It focuses on necessary water criteria to minimize operating problems with cooling tower systems such as loss of heat transfer, fouling, and corrosion.

Technical feasibility—This section evaluates the technical feasibility and economics of using degraded water for cooling towers, with emphasis on three hypothetical case studies involving process wastewater, agricultural return water, and reclaimed municipal effluent.

Environmental Impacts—This evaluation of environmental impacts associated with degraded water in wet cooling towers focuses on all streams leaving the cooling system, including cooling tower blowdown, drift, water loss to evaporation (as well as chemical constituents), and sludge generated from cooling tower treatment and/or maintenance.

Commercially Available Treatment—This description of treatment technologies required in order to use degraded water for power plant cooling focuses on three areas of treatment: pretreatment (cooling tower makeup), sidestream (treating a portion of the recirculating water), and post-treatment (blowdown).

Emerging technologies—This section identifies emerging treatment technologies for degraded and reclaimed water. These technologies focus on environmental issues such as metals, pesticides, and organic compound removal. Most are in initial stages, but show promise.

Challenges & Objectives

Two recently commissioned power plants in northern California use treated municipal effluent for cooling. In addition to reclaimed water, another project will blend treated contaminated groundwater feedwater (originally containing trace levels of volatile organic compounds) into the cooling tower. To date, however, uncertainties regarding the costs, and to a lesser extent, the environmental requirements for using degraded water for wet cooling have presented major barriers to its regular use in California power generation. The key objectives of this project were to identify potential types of degraded water, pollutants specific to these types of water, and water quality requirements necessary for cooling water. In addition, the project was designed to investigate the technical feasibility and environmental impacts of using degraded water for power plant cooling. Finally, as an outgrowth of these objectives, the project intent was to identify commercial and emerging technologies to treat degraded or reclaimed water.

Applications, Values & Use

More than 22,000 MW of new and replacement power were planned or under construction in 2001. If the currently projected new generation power plants in California used degraded water for cooling, approximately 140,000 acre-feet per year of freshwater could be diverted to other uses, according to a CEC estimate. This is equivalent to the annual water use of 545,000 people, based on an average 1995 per-capita water use in California of 229 gallons per day. If technical and environmental uncertainties surrounding the use of degraded water can be eliminated, a significant portion of nonpotable water may present viable alternative cooling water supplies.

EPRI Perspective

California's population is expected to grow by 50 percent in the next 20 years, increasing the demand and competition for freshwater. Such growth mandates freshwater conservation coupled with viable use of nonpotable water sources in power production. This report offers valuable advice on the use of degraded water sources as cooling water in power plant applications. Purposely limited to general guidance, the report conforms to the broad objectives of the CEC's Public Interest Energy Research (PIER) Program—to enhance environmental protection, lower energy costs, and improve the overall value of California's electricity.

Approach

The principle investigator relied on literature searches, personal experience, and interviews with vendors and other experts to gather information on water sources, quantities, and quality. This information was analyzed with reference to known design and operating parameters typical for cooling water systems to assess which types of design features, treatments, specialty chemicals, and disposal options would be necessary to utilize degraded sources as cooling water makeup.

Keywords

Cooling Water

Freshwater Conservation

Degraded Water Sources

ABSTRACT

In California, competing demands for freshwater have forced thermal power plant developers to consider alternative cooling water supplies. At the same time, the use of alternative or degraded water supplies for power plants is limited. Degraded water is defined in this document as surface water, groundwater, treated municipal effluent or industrial process water which is not suitable for potable use because of natural or manmade contamination. Other than treated municipal effluent, there are few (if any) developed alternate sources of degraded water used for cooling. Presently, uncertainties regarding the costs, and to a lesser extent, the environmental requirements for using degraded water for wet cooling are the major barriers to its regular use in power generation in California.

This report provides basic tools and guidelines to public and private parties involved in source water evaluations for power projects in California. *The report is purposefully limited to general guidance and is not designed to address all the possible technical areas that can arise in evaluating degraded water and its impact on conventional cooling systems.* This report conforms to the broad objectives of the California Energy Commission's Public Interest Energy Research (PIER) Program which are to enhance environmental protection, lower energy costs and improve the overall value of California's electricity.

This report encompasses the following general objectives:

- Identify potential types of degraded water, the pollutants specific to these types of water and the water quality requirements necessary for cooling water
- Investigate the technical feasibility and environmental impacts of using degraded water for power plant cooling
- Identify commercial and emerging treatment technologies to treat degraded or reclaimed water

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These acknowledgments should not be interpreted as meaning that all of the participants are in accordance with or endorse the conclusions of this study. The final report reflects the opinions and points of view of the author.

EXECUTIVE SUMMARY

Introduction

In California, competing demands for freshwater have forced thermal power plants to consider alternative cooling water supplies. Currently, the use of alternative water supplies for power plants is limited. Other than treated municipal effluent, there are few (if any) developed alternate sources of degraded water used for cooling. In 1999, reclaimed water for irrigation, groundwater recharge and industrial use in California totaled 401,910 acre feet (Municipal Wastewater Reclamation Survey, 2000). This is equivalent to average rate of use of 360 mgd (million gallons per day). Of that amount, 2.85% or 11,466 acre-feet were used for cooling tower make-up for petroleum refineries, landfill energy facilities and power plants. More than 22,000 MW of new and replacement power were planned or under construction in 2001. This is equivalent to the annual water use of 545,000 people based on an average 1995 per-capita water use in California of 229 gallons per day. It should be noted that much of the planned generating capacity and a number of projects in construction were curtailed in 2002 as a result of changing market conditions. Independent of recent project curtailments, California's population is expected to grow by 50 percent in the next twenty years increasing the demand and competition for freshwater (California Water Plan Update, Bulletin 160-98, 1998). Two recently commissioned power plants in northern California are using treated municipal effluent for cooling. In addition to reclaimed water, another project will blend treated contaminated groundwater into the cooling tower feedwater (originally containing trace levels of volatile organic compounds). Presently, uncertainties regarding the costs, and to a lesser extent, the environmental requirements for using degraded water for wet cooling are the major barriers to its regular use in power generation in California.

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Water Quality Requirements for Cooling Systems

Degraded water can be defined by many parameters, but for the purposes of this paper, it is described as non potable, i.e. groundwater or surface water impacted by naturally-occurring minerals or human impacts and wastewater generated by human, industrial or agricultural activities. Some degraded water examples follow:

- Contaminated surface water or groundwater
- Surface water impacted by agricultural activities
- Treated municipal effluent (reclaimed water)
- Produced water from oil-field operations

In assessing proposed water sources, *constituents of concern must be evaluated*. Any one constituent could eliminate a possible source or require the imposition of significant treatment. Cooling tower chemistry criteria are used to evaluate constituents of concern. Note, that some of the criteria can be considered key parameters for degraded water, i.e. PO₄ (total phosphate), Cu (copper), Al (aluminum), S (sulfide), NH₃ (ammonia), BOD (biological oxygen demand) and COD (chemical oxygen demand). There also may be chemical criteria that are specific to degraded water that have not been identified yet.

Cooling tower water quality requirements, which are guidelines used to assess potential sources of water, have not changed much during the past fifteen years. During the intervening years, a shift in the manner of treating cooling towers has occurred as a result of the elimination of chromate (Cr+6) treatment for corrosion protection in industrial cooling towers. With the move towards non-chromate treatment, pH control ranges shifted from neutral (6.5 to 7.0) to alkaline (7.5 to 8.5). The shift from chromate control was creating cooling tower operational problems and driving specialty chemical technology to meet the changing demands for scale, corrosion and biological control.

This section of the report also describes a six-step methodology that is designed for evaluating degraded or freshwater sources for suitability as make-up water to cooling towers:

1. Identify and characterize the source water(s).
2. Evaluate constituents of concern.
3. Identify cooling tower design and operating Impacts.
4. Determine the need for treatment.
5. Evaluate treatment requirements.

6. Evaluate disposal issues.

The methodology is utilized throughout the report in various formats to assess water sources, assess case studies and identify and discuss appropriate treatment options.

Four actual sources of degraded water and freshwater are screened and compared. The produced water, agricultural return water and freshwater sources are located in the Central Valley of California and the reclaimed water source in the Bay Area. Each source was evaluated based on the chemical criteria found outlined in the report. The screening analysis shows that cycles of concentration may be significantly limited by one or more constituents for each degraded water source.

For source waters that are impacted by scale, corrosion or environmental factors, there are commercially available treatment technologies that can be employed. Treatment generally falls into three categories, and depending on site-specific requirements, one, two or all three of the categories could be employed for a degraded water source. Each category is discussed generally in this section, and in greater detail, later in the report. Pre-treatment can be utilized to remove contaminants, adjust pH, soften (remove calcium and magnesium), reduce silica or reduce TSS. Side-stream can be used to soften, reduce silica or reduce TSS. Lastly, Post treatment is utilized to reduce blowdown volume (e.g. zero discharge) or meet discharge requirements.

Lastly, the regulatory framework and specific rules, which apply to steam-electric power plant cooling in California, are also reviewed in this section. The discussion is confined to wet evaporative cooling with particular emphasis on those elements which would be most affected by the use of degraded water for cooling tower make-up. *Environmental issues related to new power projects are numerous and complex. The information is presented in a generalized manner and is intended to identify issues of concern rather than specific regulatory requirements.*

Technical Feasibility

Technical feasibility and economics of using degraded water for cooling towers is evaluated in this section. Three hypothetical case studies of power plants using degraded water for cooling are discussed and evaluated in detail. The case studies include process wastewater, agricultural return water and reclaimed municipal effluent. Water consumption, water treatment equipment, chemicals requirements, cooling tower blowdown, solid-waste generation, operating costs and order-of-magnitude capital costs are identified for each case study. All case studies are evaluated against freshwater for comparative purposes and to benchmark the cost analysis.

The degraded water scenarios that are evaluated in the report are admittedly “difficult” from a freshwater treatment perspective, but as illustrated by the case studies, they are usable with appropriate treatment. Three degraded water case studies are evaluated in this section of the report:

- Produced water - saline process wastewater generated by oil production

-
- Agricultural return water - saline water generated by flood irrigation
 - Reclaimed water - treated municipal effluent generated in urban areas

Operating data, treatment equipment requirements, chemical and power consumption, sludge production, dedicated labor and operating and capital costs developed for all the scenarios are summarized in detail. The rationale for waste treatment selection is discussed in the applicable sections of this report. The daily operating cost which includes consumables, labor and amortization is also determined. *The summary shows that water costs associated with degraded water are at least 1.5 to 2.5 times the costs associated with fresh water at inland plants and 1.1 to 1.2 times that of fresh water at coastal plants (based on assumed water chemistries, Table 3-1, and the evaluation basis, Table 3-2).* These ranges could be broader/narrower depending on the quality of the water source. Generally speaking, the greater the TDS, hardness and silica of the degraded source water, the greater the ratio.

Environmental Impacts

Environmental impacts can originate from a variety of cooling tower streams and activities associated with the cooling circuit:

- Evaporation
- Drift
- Blowdown
- Waste streams from treatment processes associated with the cooling circuit
- Sludge generated from cooling system maintenance

All of these streams have the potential of transporting chemical constituents of concern and producing environmental impacts.

When degraded water is employed for make-up, cooling tower evaporation can contain gaseous contaminants in addition to water vapor, e.g. trace levels of volatile organic compounds. Depending on the source water, constituents of concern, such as trace levels of heavy metals and organic compounds, could also be found in the circulating cooling water. Since drift and blowdown are component streams of circulating water, they contain all of its chemical constituents. Biological pathogens such as *Legionella pneumophila*, which can thrive in cooling water systems and are transported via drift, pose a potential human health concern. Treatment processes, such as side-stream filtration and softening, evaporators and crystalizers, generate liquid, sludge and solid waste streams which are comprised of circulating water and its constituents - chemical compounds, particulate matter, biological material and treatment chemical byproducts. Lastly, sludge from cooling tower maintenance contains inorganic, organic and biological sediments generated by day-to-day operation. This section of the report discusses potential environmental impacts related to airborne and waterborne contaminants, water quality issues related to the disposal of blowdown and treatment process wastes, and safety as it relates to working in and around cooling towers.

Legionella pneumophila, which is the bacterium responsible for the well-documented outbreak of “Legionnaires’ Disease” in 1976, is discussed in some detail. *Legionella* can originate from a number of industrial and commercial sources including cooling towers and evaporative condensers. In the case of cooling towers, the pathway is drift - fine droplets or mist in the aerosol-size range carrying viable *Legionella* bacteria. OSHA estimates over 25,000 cases of the illness occur every year in the United States. More than 4,000 deaths are believed to occur, but only a fraction are reported. About 1,400 cases of Legionellosis are reported to the Center for Disease Control (CDC) annually and about 500 are confirmed. *Legionella* is transmitted by breathing aerosol-sized droplets of water that contain the bacteria. It is estimated that Legionellosis is fatal to 10 to 20 percent of those who contract it and much higher for at-risk individuals.

Drift droplets from cooling towers containing *Legionella* bacteria must survive ambient conditions and not evaporate to be a threat to human health. Ambient air conditions that include low relative humidity will likely evaporate aerosol-sized drift droplets shortly after they exit the cooling tower. Larger drops exposed to air with low relative humidity could evaporate and shrink sufficiently to enter the alveoli. Conversely, under high-humidity conditions, drift aerosols could be carried for some distance, thus posing a potential health risk in urban areas or commercial/industrial parks. Drift poses more of a threat to individuals who work in the immediate vicinity of a cooling tower.

Hyperlink addresses to the full texts of *Legionella* guidelines and position papers prepared by the Cooling Technology Institute (CTI) and American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) are found in Appendix A.

Worker safety issues, which are also touched upon, can arise when working in and around cooling towers and related treatment equipment such as make-up and side-stream process treatment. Worker safety issues include (but are not limited to):

- Legionellosis
- Exposure to untreated degraded water containing volatile compounds, pesticides, heavy metals, hydrogen sulfide, etc.
- Biological control chemicals such as chlorine and bromine compounds
- Specialty chemicals used for scale and corrosion control
- Chemicals (as well as waste streams) generated by water treatment equipment such as sulfuric acid, sodium hydroxide, hydrated lime, etc.
- Maintenance wastes such as biological sediments

Tools are available to assess Legionellosis and workplace hazards. In addition to the CTI guidelines and ASHRAE position paper, OSHA has an entire section of its technical manual dedicated to Legionnaire’s Disease, Section III, Chapter 7. There is also a section on assessing and documenting Legionellosis cases, OSHA Appendix III:7-5, Water Treatment Protocols for Facilities That Have Experienced a Legionnaires’ Outbreak.

Commercially Available Technology

Degraded water sources potentially could contain a variety of chemical constituents that must be removed prior to use as cooling tower make-up. Treatment categories discussed in this section include:

- Air stripping followed by vapor-phase granular activated carbon (GAC) for the removal of regulated volatile organic compounds, THMs and some pesticides
- Air stripping followed by vapor-phase thermal oxidation for the removal of regulated volatile organic compounds, THMs and some pesticides
- Liquid-phase GAC for the removal of regulated volatile and non-volatile organic compounds (including pesticides) and incidental removal of some BOD and some COD
- Aerobic biological treatment for the removal of organic compounds and ammonia and incidental removal of BOD and COD.
- Anaerobic biological treatment for the removal of many organic compounds, AsO_4^{-3} , CrO_4^{-2} , SeO_4^{-2} , SeO_3^{-2} and ClO_4^{-1} (arsenate, chromate, selenate, selenite and perchlorate) and incidental removal of BOD, COD, possibly NO_3^{-1} , etc.
- Strong-base anion ion exchange for the removal of AsO_4^{-3} , CrO_4^{-2} , SeO_4^{-2} , SeO_3^{-2} and ClO_4^{-1} and incidental removal of PO_4^{-3} (ionic species), NO_3^{-1} and F^{-1}
- Chelating ion exchange for the removal of Cu, Ni, Cd, Cr^{+3} , etc.
- Precipitation for the removal of Cu, Ni, Cd, Cr^{+3} , AsO_4^{-3} , CrO_4^{-2} , SeO_3^{-2} and incidental removal of PO_4^{-3} and F^{-1} (under certain conditions)

In addition to the above technologies, “traditional” pre-treatment and side-stream treatment technologies, such as lime-soda softening, are also discussed in this section. Post treatment in the form of blowdown reduction is usually considered for inland plants where disposal options are limited to evaporation ponds. Evaporators can be installed in conjunction with make-up or side-stream softening to minimized blowdown and thus the evaporator (and crystallizer) size. Two forms of post-treatment are being utilized in California, evaporators and evaporator-crystallizer process combinations. Installed costs for softening, evaporators, crystallizers and evaporation ponds are discussed in the section.

Costs were not estimated for remediation technologies . This analysis is not within of the scope of this report because of the process uncertainties created by the very large range of constituents to be removed and the treatment variables associated with desired or regulated effluent concentrations.

Operating costs are presented for make-up and side-stream reactor clarifiers which use lime and soda ash to soften water (silica is also removed). The operating costs which include lime, soda ash and polymer, cover a large range of feedwater hardness and alkalinity. A method of determining sludge generation is also provided.

Emerging Technologies

Emerging treatment technologies and processes that may make it possible to use degraded and reclaimed water are identified. An effort was made to identify processes not considered in the mainstream of treatment approaches. The technologies in this section focus primarily on environmental contaminants typically associated with degraded water - heavy metals, pesticides and organic compounds. One technology involves de-ionization (salinity reduction). Many of the technologies are in the early phases of research and development and some are commercial. Contact information is provided for each technology.

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1

INTRODUCTION

1.1 Objective of the Report

In California, competing demands for freshwater have forced thermal power plants to consider alternative cooling water supplies. Currently, the use of alternative water supplies for power plants is limited. Other than treated municipal effluent, there are few (if any) developed alternate sources of degraded water used for cooling. In 1999, reclaimed water for irrigation, groundwater recharge and industrial use in California totaled 401,910 acre feet (California Department of Water Resources, 2000). This is equivalent to average rate of use of 360 mgd (million gallons per day). Of that amount, 2.85% or 11,466 acre-feet were used for cooling tower make-up for petroleum refineries, landfill energy facilities and power plants. Only 436 acre-feet per year (0.39 mgd) of reclaimed water was used for power plant cooling. Note, the power plants using reclaimed water in the survey have been doing so for a significant period of time. If the currently-projected new generation in California used degraded water for cooling, approximately 140,000 acre-feet per year of freshwater could be diverted to other uses based on a California Energy Commission (CEC) estimate. More than 22,000 MW of new and replacement power were planned or under construction in 2001. (CEC, 2000) This is equivalent to the annual water use of 545,000 people based on an average 1995 per-capita water use in California of 229 gallons per day. California's population is expected to grow by 50 percent in the next twenty years increasing the demand and competition for freshwater (California Water Plan Update, Bulletin 160-98, 1998). Two recently commissioned power plants in northern California are using treated municipal effluent for cooling. In addition to reclaimed water, another approved project will blend treated contaminated groundwater into the cooling tower feedwater (originally containing trace levels of volatile organic compounds). Presently, uncertainties regarding the costs, and to a lesser extent, the environmental requirements for using degraded water for wet cooling are the major barriers to its regular use in power generation in California.

This report provides basic tools and guidelines to public and private parties involved in source water evaluations for power projects in California. *The report is purposefully limited to general guidance and is not designed to address all the possible technical areas that can arise in evaluating degraded water and its impact on conventional cooling systems.* This report conforms to the broad objectives of the CEC's Public Interest Energy Research (PIER) Program which are to enhance environmental protection, lower energy costs and improve the overall value of California's electricity.

This report encompasses the following general objectives:

- Identify potential types of degraded water, the pollutants specific to these types of water and the water quality requirements necessary for cooling water
- Investigate the technical feasibility and environmental impacts of using degraded water for power plant cooling
- Identify commercial and emerging treatment technologies to treat degraded or reclaimed water

1.2 Report Scope of Work

In the production of electricity, almost all thermal power plants reject heat either to a large body of water (e.g. once-through cooling) or the atmosphere via wet cooling towers. Evaporative or wet cooling towers, which are the predominant form of cooling in California, use considerable quantities of water. For example, a 500 MW combined cycle plant (with approximately 33 percent of its power originating from steam generation) evaporates 2,500,000 gallons of water to the atmosphere per day. The competitive pressures associated with using freshwater for power generation are growing and many projects, which are now in the planning stages, are seriously considering dry cooling. Currently, there are three operating dry cooling systems in California (a total of approximately 800 MW of power), one project planning to use dry cooling is on hold, and a number of new projects are reviewing this alternative. In addition to dry cooling, one project is planning to install a wet/dry hybrid cooling tower. Alternative water supplies offer significant opportunities for power plants to limit their use of freshwater. However, there are uncertainties within the power community regarding the costs and environmental impacts of using degraded water for cooling. Note that degraded water is defined in this document as surface water, groundwater, treated municipal effluent or industrial process water/wastewater which is not suitable for potable use because of natural or manmade contamination. Additionally, the availability and quality of degraded water supplies have not been assessed or characterized in California. Potential sources of degraded water include: contaminated groundwater, treated municipal effluent, industrial process water or wastewater, irrigation return water, brackish water, etc. The report is organized into the following sections.

1.2.1 Water Quality Requirements for Cooling Systems

Water quality criteria, which have evolved over the past 40 to 50 years, are utilized by the power industry and others to minimize operating problems with cooling tower systems such as loss of heat transfer, fouling and corrosion.

Prior to discussing water quality requirements for cooling systems, this section of the report introduces a Source Water Evaluation Methodology to assess degraded and freshwater sources water for cooling tower make-up. The methodology is a six-step evaluation of source water chemistry, chemical criteria for cooling towers, cooling system design and operating impacts, source water screening, treatment requirements and disposal issues. The methodology provides a stepwise framework for the systematic evaluation of degraded water for cooling tower make-up. Elements of the methodology are utilized throughout the report.

Water quality criteria for cooling towers are presented. The cooling system is defined and associated operating issues and concerns are discussed, e.g. scaling, corrosion and biological fouling. To evaluate degraded water for cooling, it is first categorized into types, e.g. contaminated groundwater, reclaimed water, agricultural return water, etc. Pollutant types commonly found in degraded water are identified by category, e.g. volatile organic compounds, heavy metals, high levels of background salt, etc. The concept of cooling water cycles of concentration is introduced - this parameter is central to all source water evaluations. The determination of cycles of concentration is presented and its impact on water consumption and wastewater generation is discussed. Water quality criteria are then utilized to screen and evaluate several degraded water sources. Water quality requirements are also applied to freshwater to enable freshwater versus degraded water comparative analysis. Cooling water treatment requirements and waste disposal issues are briefly discussed in this section. Environmental rules and regulations are identified for each applicable cooling tower stream (e.g. blowdown, evaporation, etc.) and generally discussed.

1.2.2 Technical Feasibility

The technical feasibility and economics of using degraded water for cooling towers is evaluated in this section. Three hypothetical case studies of power plants using degraded water for cooling are discussed and evaluated in detail. The case studies include process wastewater, agricultural return water and reclaimed municipal effluent. Water consumption, water treatment requirements, cooling tower blowdown, disposal requirements, operating cost and order-of-magnitude capital cost. All case studies are then evaluated against freshwater for comparative purposes and to benchmark the cost analysis.

1.2.3 Environmental Impacts

Environmental impacts associated with degraded water in wet cooling towers are identified. These include an evaluation of all streams leaving the cooling system, i.e. cooling tower blowdown, drift, water loss to evaporation (as well as chemical constituents) and sludge generated from cooling tower treatment and/or maintenance. The rules and regulations discussed in Section 2, Water Quality Requirements for Cooling Systems, frame each area of environmental impact. Impacts such as surface and groundwater contamination, salt deposition from drift, Legionnaires Disease, vapor emissions from volatile organic chemicals, trihalomethane (THM), etc. are discussed. Occupational safety is discussed as it relates to the daily exposure of working in and around cooling towers.

1.2.4 Commercially Available Treatment

Treatment technologies that are required in order to utilize degraded water for power plant cooling are identified in this section. Three areas of treatment are investigated: pre-treatment (cooling tower make-up), side-stream (treating a portion of the recirculating water) and post-treatment (blowdown). The technologies comply with the following criteria: generate minimal

environmental impact (hazardous process chemicals, waste, noise, etc.) and are commercially-available off-the-shelf technology. Technologies are also sorted into two areas: those required to remediate specific environmental problems and those required to maintain plant performance.

1.2.5 Emerging Technologies

Emerging treatment technologies and processes that may make it possible to use degraded and reclaimed water are identified. The technologies in this section primarily focus on environmental issues - metals removal, pesticide removal and organic compound removal. One technology covers de-ionization (salinity reduction). Most of the technologies are in initial phases of research and development but show promise.

2

WATER QUALITY REQUIREMENTS FOR COOLING SYSTEMS

2.1 Introduction

This section of the report lays the foundation for all of the subsequent sections. Before water quality requirements of cooling towers are discussed, a six-step Source Water Evaluation Methodology is presented. The methodology is a tool designed to analyze the feasibility of using degraded water as well as freshwater sources.

2.1.1 Source Water Evaluation Methodology

In evaluating degraded or freshwater sources for suitability as make-up water for cooling towers, a systematic means of evaluation should be used. Refer to Figure 2-1 for a depiction of the six steps and the miscellaneous inputs which comprise the methodology.

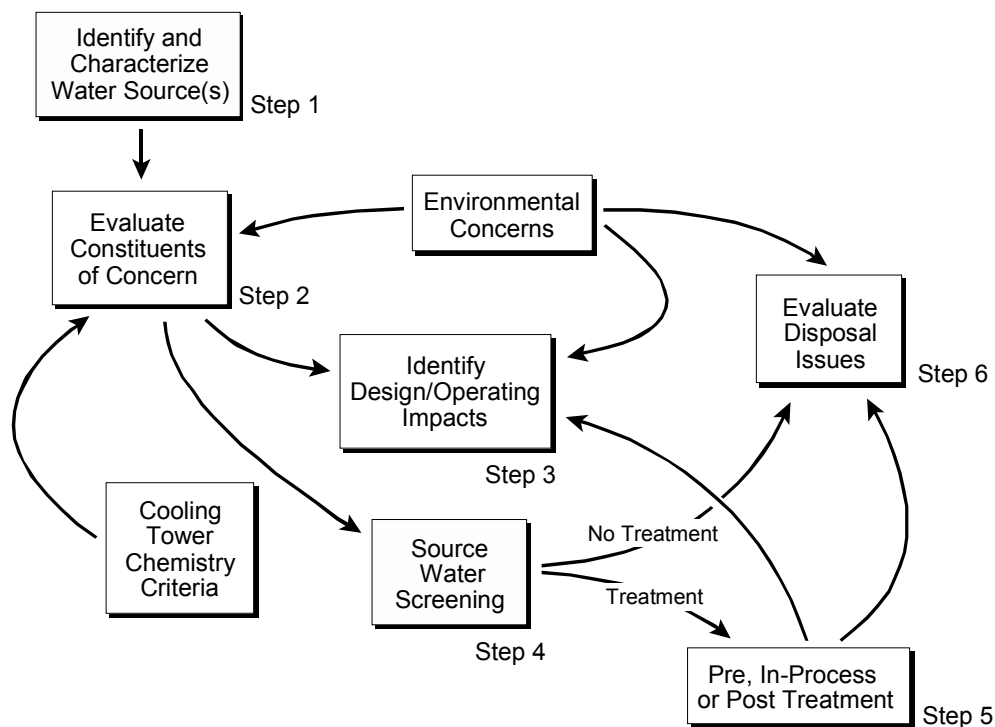


Figure 2-1
Source Water Evaluation Methodology

Step 1. Identify and Characterize the Source Water(s). The process starts with chemical analyses and flow profiles of the source. The analyses should include constituents identified in Tables 2-1 and 2-2 as well as chemical constituents specific to Water Quality Objectives set forth by the Regional Water Quality Control Board (RWQCB). Refer to 2.4 Environmental Rules and Regulations. Flow profiling is very useful for projects with multiple sources of water, especially when flow capacity or yield is suspect for one or more sources. If more than one source is to be used (because of inadequate flow or yield), complete analyses and blend calculations should be performed to predict nominal- and worst-case make-up water quality variability. *The data generated in this analysis will define the basis for evaluating the feasibility of a degraded water source, therefore it must be thorough.* The following rules of thumb should be applied when establishing source water chemistry for degraded source water:

- Surface water - at least one year of seasonal chemistry should be obtained, i.e. twelve months of data.
- Contaminated groundwater - general mineral chemistry should be almost constant with slight changes in concentration annually, therefore one complete chemical analysis should suffice. If historic groundwater data is available, it should be carefully reviewed to note possible trends in key constituents. Contaminant concentrations could be mobile, i.e. changing with time as a result of groundwater movement. Typically these types of contamination cases are under study and are in the process of characterization. Since contaminants will more than likely require removal prior to cooling tower use, conservative values for contaminants should be considered.
- Reclaimed municipal wastewater - a minimum of one year of seasonal data. Unless a municipal wastewater plant has been involved in reclamation for industrial reuse, useful water quality data will not be available. Composite samples taken every hour over a period of 24 hours are preferred because water quality (and flow) is diurnal at sewage treatment plants. Summer or dry-month chemistry usually represents the “worst case” scenario for reclaimed water (highest concentrations of chemical constituents and lowest flows). Also daily volumes of treated effluent are usually at a minimum during the summer months.
- Other degraded water sources - at least one year of monthly chemistry should be obtained. For industrial wastewater, the chemistry should be established based on 24-hour composite sampling because of possible flow and chemistry variations.

For these and other degraded waters, more data yields more confidence in the water analysis.

Step 2. Evaluate Constituents of Concern. This is a two-part step. It includes a constituent-by-constituent review of chemical analyses for conformance to the cooling tower criteria found in Table 2-1 (derivation of criteria discussed next) and an assessment of environmental concerns. Refer to Figure 2-1.

2.1.2 Cooling Tower Chemistry Criteria

Each chemical constituent (in some cases, constituent pair) that can effect cooling system performance must be evaluated separately to determine its maximum allowable concentration in the cooling system. Table 2-1 shows an evolution of published cooling water criteria over the past 23 years (Kunz, 1977, EPRI, 1982, EPRI, 1998, Eble, 1993). The criteria in the first three columns are applicable to power plants and the last column for oil refineries.

These criteria are shown because they differ significantly from most power plant cooling parameters. Cooling systems in refineries are typically smaller and are usually not tied to overall plant efficiency. Therefore, they have higher limits and “push” their cooling systems harder. Cooling systems at power plants can significantly effect steam cycle performance so operating criteria are more conservative. Also, the criteria for refineries include constituents not typically found in traditional cooling tower criteria for power plants, but are found in degraded water, e.g. BOD and COD (the cited reference includes numerous other criteria). *The criteria found in column three of Table 2-1, which were developed by EPRI in 1998, are the most recent and should be used in cooling tower evaluations.* Table 2-1 is also discussed in 2.3.3 Impacts of Chemical Constituents on Water Consumption, Source Selection and Waste Generation. One or more constituents will usually define the concentration limit for the cooling system. The limit pertains to solubility, e.g. a calcium limit can refer to the calcium sulfate solubility threshold. If the limit is exceeded, calcium sulfate will likely precipitate. Understanding the variability of water source(s) chemistry, as discussed in Step 1 above, is crucial in identifying all the possible solubility limitations.

Table 2-1
Cooling Tower - Water Quality Parameters

<i>Degraded Water TC</i>				Current EPRI⁽¹³⁾ Standards 1998	Refinery Cooling System ⁽¹³⁾ 1993 ⁽⁹⁾
Parameter	Units	Kunz ⁽¹³⁾ 1977	EPRI ⁽¹³⁾ 1982		
Ca	mg/l _{CaCO3}	300	900 (max)	(Note 6)	1,500 (max)
Ca x SO ₄	(mg/l) ²	500,000	-----	500,000 ⁽⁵⁾	(Note 10)
Mg x SiO ₂	mg/l _{CaCO3} x mg/l _{SiO2}	-----	35,000 ⁽²⁾ 75,000 ⁽³⁾	35,000 ⁽⁵⁾	-----
M Alkalinity	mg/l _{CaCO3}	-----	30-50 ⁽²⁾ 200-250 ⁽³⁾	(Note 6)	-----
SO ₄	mg/l	-----	-----	(Note 6)	5,000 (max)
SiO ₂	mg/l	150	150	150 ⁽⁵⁾	300 (max)
PO ₄	mg/l	-----	<5 (Note 4)	(Note 6)	50 (max)
Fe (Total)	mg/l	0.5	-----	<0.5 ⁽⁵⁾	10 (max)
Mn	mg/l	0.5	-----	<0.5	1
Cu	mg/l	0.08	-----	<0.1	0.5
Al	mg/l	1	-----	<1	1
S	mg/l	5	-----	5	10
NH ₃	mg/l	-----	-----	<2 ⁽¹²⁾	40 (max)
pH		8.0 (max)	6.8-7.2 ⁽²⁾ 7.8-8.4 ⁽³⁾	(Note 6)	7-9
TDS	mg/l	2,500	70,000	-----	-----
TSS	mg/l	100-150	-----	<100 ⁽⁷⁾ - <300 ⁽⁸⁾	200
BOD	mg/l	-----	-----	-----	200 (max)
COD	mg/l	-----	-----	-----	200 (max)
Langelier SI ⁽¹¹⁾		+1.5 (max)	-----	<0	-----
Ryznar SI ⁽¹¹⁾		+7.5 (max)	-----	>6	-----
Puckorius SI ⁽¹¹⁾		-----	-----	>6	-----

Notes.....

1. M Alkalinity = HCO₃ + CO₃, expressed as mg/l_{CaCO3}.
2. Without scale inhibitor.
3. With scale inhibitor.
4. No recommendation given because of insufficient data.
5. Conservative value - reference is made to EPRI's SEQUIL RS for predicting case-specific limits. SEQUIL RS takes into account parameters such as ionic associations, ionic strength (measure of background salt and ionic charge), pH and temperature to predict the solubility of certain salts.
6. No value given - reference is made to EPRI's SEQUIL RS for predicting case-specific limits.
7. <100 mg/l TSS with film fill.
8. <300 mg/l TSS with open fill.
9. Water quality parameters were prepared by Betz for refinery cooling towers accepting in-plant wastewater as a means of conserving water. Refineries typically experience more severe operating conditions than power plants, e.g. higher temperatures, organic contamination, heavy metals, etc.
10. No inference was made by the authors to the product of the Ca and SO₄ maximum operating values to be used to set a Ca x SO₄ limit (reference Kunz and EPRI values).
11. Refer to Appendix B for a discussion of the Langelier, Ryznar and Puckorius calcium carbonate saturation indices.
12. <2 mg/l NH₃ applies when copper bearing alloys are present in the cooling system. This does not apply to 70-30 or 90-10 copper nickel.
13. Refer to citations 4, 5, 6 and 7 found in Appendix A.

For each constituent of concern found in Table 2-1, calculate the maximum cycles of concentration (N). N is a universal measure that not only defines the maximum concentration for a limiting chemical constituent but is also used to determine critical cooling tower operating conditions - make-up and blowdown rates.

$$N = \frac{C_{Limit}}{C_{MU,i}} \quad (1)$$

Where: N Cycles of concentration
 $C_{Limit,i}$ Water quality limit for constituent i
 $C_{MU,i}$ Concentration of constituent i in the make-up water

For ion pair limits such as magnesium and silica, calculate the maximum cycles of concentration as follows:

$$N = \sqrt{\frac{C_{Limit,ij}}{C_{MU,i} C_{MU,j}}} \quad (2)$$

Where: $C_{Limit,ij}$ Water quality limit for constituents i and j
 $C_{MU,i}$ Concentration of constituent i in source water
 $C_{MU,j}$ Concentration of constituent j in source water

After this calculation has been completed for each of the constituents of concern, the constituent or constituent pair with the lowest calculated N value will be the limiting parameter for that source of water or blend of source waters. This value of N will be the maximum cycles of concentration achievable without some form of pretreatment or side-stream treatment or specialty chemical addition (e.g. scale inhibition).

2.1.3 Environmental Constituents of Concern

For degraded water, environmental concerns could include volatile organic solvents, pesticides, heavy metals, etc. Refer to Table 2-2. This table categorizes types of degraded water and the chemical constituents likely found in those waters. As stated previously, the availability and quality of degraded water supplies have not been assessed or characterized in California. This table is also discussed in more detail in 2.3.3. Many of the compounds found in degraded water (e.g. volatile organic compounds) have no measurable effect on cooling tower performance, but they are strictly regulated for environmental reasons. Therefore, it is likely that many of these regulated compounds will have to be removed from the feedwater prior to use in the cooling tower. Lastly, the cycles-of-concentration calculation outlined above should be applied to all degraded water constituents.

Table 2-2
Degraded Water Categories

	General Minerals (Note 3)	Biological (Note 4)	Organic Compounds (Note 5)	Metals (Note 6)	Other (Note 7)
Fresh water ⁽⁸⁾	†		(Note 10)	(Note 10)	
Reclaimed water	†	†	(Note 10)	(Note 10)	†
Industrial process water ⁽⁹⁾	†	†	†	†	†
Degraded water					
⌚ Agricultural return water ⁽¹⁾	†	†	†	†	†
⌚ Dairy or feed-lot runoff	†	†	†		†
⌚ Brackish water ⁽²⁾	†			†	†
⌚ Contaminated groundwater	†		†	†	†

Notes.....

1. Selenium has been identified as a heavy-metal contaminant in some agricultural tailwaters.
2. Surface or groundwater with TDS >1,500 mg/l.
3. General Minerals Na, K, Ca, Mg, HCO₃, CO₃, Cl, SO₄ and SiO₂.
4. Biological BOD, COD, NH₃, PO₄, etc. Typically found in reclaimed wastewater as well as pharmaceutical, biotech, livestock/dairy and food processing waste streams.
5. Organics Volatile, non-volatile or pesticide compounds.
6. Metals Ba, Sr, Fe, Mn, Cu, Zn, Se, As, Cr, Hg, etc.
7. Other NO₃, PO₄, ClO₄, S, F, etc.
8. Can be surface water or groundwater. Many supplies contain trace levels of organic compounds and metals.
9. Examples are produced water (oil production), micro-electronics wastewater, mine sluice water, electroplating rinse water, etc.
10. Trace concentrations of organics and metals (within regulatory limits) are found in many fresh water supplies.

Specialty chemicals that inhibit scale formation, biological fouling and corrosion in cooling systems play a important role in the industrial sector. These chemicals are usually applied in combinations to manage and control a number of possible problems, e.g. corrosion, scale, fouling, etc. There are several large and many small companies that provide these chemicals along with services to monitor and maintain chemical treatment levels. Because of this diversity of products and product combinations, it is not possible to incorporate the benefits and impacts of specialty chemicals for each criteria presented in Table 2-1. However, the lowest value of N calculated previously will be conservative, and with the aide of specialty chemicals, the cycles of concentration could be increased.

Step 3. Identify Cooling Tower Design and Operating Impacts. After the water source(s) has been selected and the maximum cycles of concentration have been established, cooling tower design and operating impacts should be identified. Some examples follow:

- If the feedwater contains high level of suspended solids, a wide-spaced film fill should be considered for the cooling tower to prevent fouling. Side-stream filtering and multi-point chlorination may also be needed.

- If the total dissolved solids (TDS) of the water is above 10,000 mg/l, then copper bearing alloys should be considered for the main condenser.
- If reclaimed water is used for cooling tower make up, a two-component multi-point biocide program may be required, e.g. chlorination at the condenser inlet and the use of a non-oxidizing organic biocide prior to the cooling tower fill. A mechanical condenser tube cleaning system should be considered if treated effluent quality is highly variable, e.g., Amertap®.

All of the above considerations impact the capital and operating cost of the cooling system (as with freshwater systems) and must be considered when evaluating degraded water.

Step 4. Determine the Need for Treatment. This step is usually driven by two factors: achievable cycles of concentration and constituents that create environmental concerns. For example, if it is determined that the maximum cycles of concentration is limited to 2.5 based on source water silica concentration, the make-up water rate to the cooling tower will be 166 percent of the evaporation rate (calculation discussed later). Typically, the minimum N for a cooling system is 4.5 to 5.5 cycles of concentration (also discussed later). Therefore, if the cooling tower evaporation rate is 1,750 gpm, the source water make-up rate will be 2,900 gpm and the blowdown rate will be 1,150 gpm. Depending on the power plant setting, a large blowdown rate may be completely unacceptable. Also, the source(s) of water may not support the high make-up rate. This scenario will require evaluating treatment alternatives to increase cycles of concentration and reduce wastewater disposal volume. Environmental constituents of concern may require removal before the source water is fed to the cooling tower. For example, if the degraded source water originates from an aquifer contaminated with MTBE (a gasoline oxygenate), the water will require treatment prior to feeding it to the cooling tower. If not treated, the tower will volatilize almost all of the MTBE with residual amounts leaving the tower in the blowdown - creating two environmental impacts. This scenario will also generate treatment disposal issues (discussed in Step 6, Evaluate Disposal Issues).

Step 5. Evaluate Treatment Requirements. Pre-, side-stream or post-treatment requirements depend on the constituent(s) of concern in the source water. For example, in the silica scenario discussed in Step 4, side-stream lime or lime-soda softening will be required to reduce silica concentration in the circulating water. Some power projects are choosing blowdown treatment via an evaporator/crystallizer instead of softening because there is no sludge handling, in some cases it completely eliminates the blowdown stream, it generates condensate-quality reusable water and process control is much more reliable. In the MTBE example, activated carbon or sorbent resin would be used to treat the make-up stream to the tower. The sorbent resin would have to be regenerated on site and a concentrated stream of MTBE would have to be disposed of or recycled. The carbon could also be regenerated on site, but it will likely be removed to an off-site treatment facility and replaced with fresh carbon when spent. Commercially available treatment will be discussed in Section 5 of the report.

Step 6. Evaluate Disposal Issues. Disposal issues usually revolve around cooling tower blowdown and treatment waste streams. The volume of the waste stream(s) and chemical

characteristics define the extent of the disposal issue. All of the evaluations prior to this step impact disposal issues. The lower the cycles of concentration, the greater the volume of waste. As stated previously, large waste volumes pose significant problems for plants with no convenient or environmentally-acceptable means of liquid disposal. Also, Water Quality Objectives set forth by the local RWQCB may preclude any type of disposal (discussed later in this section). Conversely, a high cycles of concentration waste stream with elevated concentrations of source-water constituents may also pose disposal problems. For example, many municipal wastewater plants will not accept high-TDS wastewater, because it impacts their allowable discharge limit of dissolved salts and possibly their water recycling programs.

2.2 Cooling Tower Operating Issues and Concerns

Interestingly, cooling tower water quality requirements have not changed much during the past fifteen years. In the mid-1980's the Electric Power Research Institute (EPRI) evaluated water quality requirements for cooling systems among other related topics. During that time, a shift in the manner of treating cooling towers was occurring. There was significant pressure from regulators to eliminate chromate (Cr+6) from industrial cooling towers (refer to Section 2.4.3.3.a, Federal Regulations) because of its carcinogenicity. Substitute metal-based corrosion inhibitors were being evaluated as well as non-metal inhibitors. Scale from mineral precipitation was typically not a problem since most cooling towers were operated at relatively low pH (6.5 to 7.5). With the move towards non-chromate treatment, pH control levels shifted upward (7.5 to 8.5) and new treatment approaches were being developed, e.g. molybdate and organic corrosion inhibitors and organic scale inhibitors. The shift from chromate control was driving specialty chemical providers to meet the changing demands for scale, corrosion and biological control.

2.2.1 Cooling Tower Function and Operation

Make-up water is fed to the cooling tower to compensate for losses from evaporation, drift (sometimes known as windage) and blowdown. See Figure 2-2. Open recirculating cooling towers reject heat mostly from the evaporation of circulating water (approximately 1,000 BTUs of heat are released per pound of water evaporated). As air is forced through the body of the tower, it passes through a shower of droplets and across films of circulating water. As the relatively dry air contacts the water, it is humidified by accepting a small amount of water. The humidified air comprises cooling tower evaporation. As circulating water is evaporated, the mineral content remains (this also applies to TSS, non-volatile organic compounds, etc.) and the concentration of salts in the circulating water increases. Blowdown is used to bleed salt from the cooling tower to prevent excess mineral accumulation and deposition. If the concentration of certain salts exceeds solubility, precipitation will occur. The blowdown rate of the cooling tower is regulated to release an equivalent amount of salt that is added via make-up water (at a much lower concentration). Drift consists of droplets of circulating water that are entrained in the cooling air.

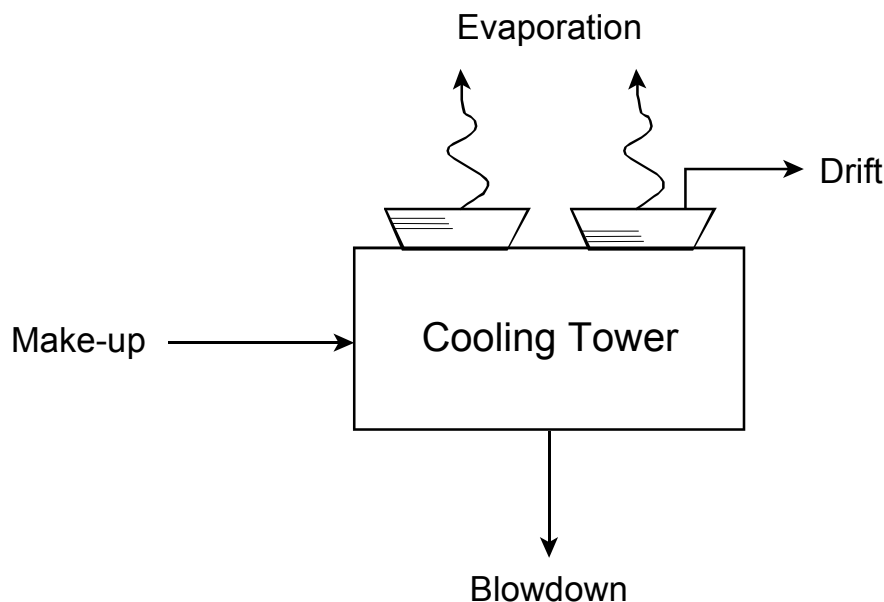


Figure 2-2
Cooling Tower Mass Balance

A simplified mass balance follows:

$$\text{Salts added by make-up} = \text{Salts lost to blowdown} + \text{Salts lost to drift}$$

The amount of water lost to drift is controlled via drift eliminators. Cooling tower manufacturers claim to achieve a drift rate of 0.002 to 0.004 percent of circulating rate. Actual drift rate may be higher in older or poorly maintained cooling towers. For a 500 MW combined cycle plant with a circulating rate of 240,000 gpm, the drift rate would be 5 to 10 gpm. The make-up rate is set to compensate for the water losses from the cooling tower. A simplified water balance follows:

$$\text{Make-up} = \text{Evaporation} + \text{Blowdown} + \text{Drift}$$

The cooling system is defined as the cooling tower, circulating water piping, main condenser(s), circulating water pumps and the cooling tower basin. In other words, all the components of cooling loop are included in the definition of cooling system. Circulating water may also serve auxiliary heat exchangers for lube oil cooling, bearing cooling water, etc.

2.2.2 Operating Issues

The objectives of water quality criteria for cooling towers are based on practical considerations:

- Minimize mineral scaling and biological fouling of heat transfer surfaces
- Minimize corrosion of heat transfer and structural metal
- Minimize fouling loads on cooling tower fill

The term “minimize” is purposefully used because none of these phenomena can be completely prevented. Four areas of water quality concern are identified in Figure 2-3: scale, suspended solids, biological fouling and corrosion. Each area generates operating problems (alone and in combination) in cooling systems, such as loss of heat transfer, fouled cooling tower fill, structural failures and tube leaks. (Lisin, 1994) For example, certain mineral scales can form on the main condenser tubes in the presence of microbiological activity resulting in a loss of heat transfer and under-deposit corrosion. Microbiologically induced corrosion (MIC) occurs at the interface of a biological film and the metal surface. (EPRI, 1987) Generally, metabolic byproducts of biological activity react with the metal surface and can initiate a number of corrosion mechanisms.

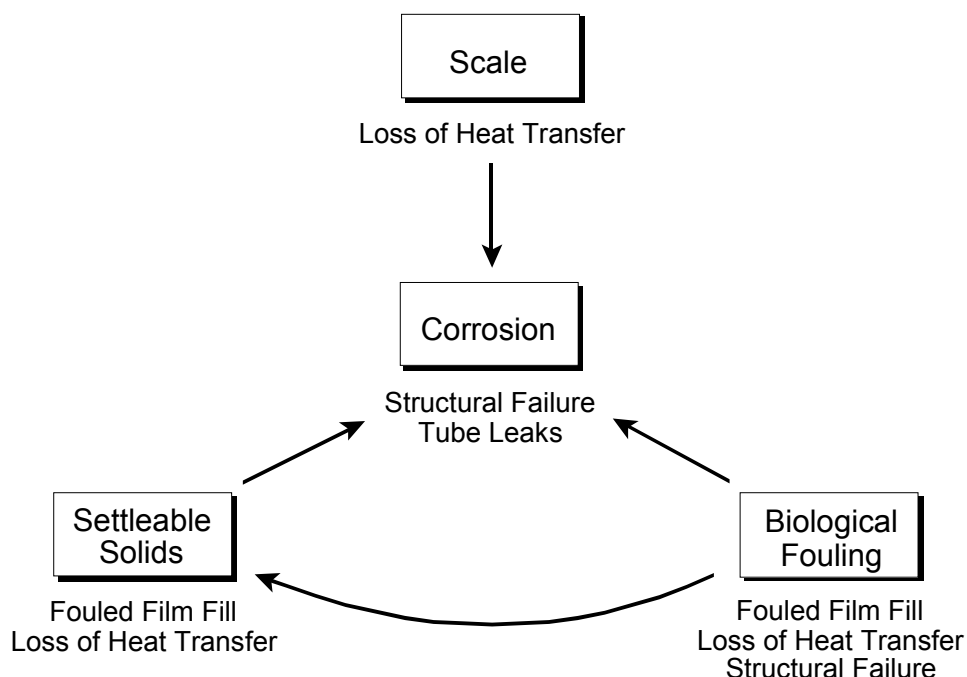


Figure 2-3
Cooling Tower Issues of Concern

2.2.3 Cooling Tower Emissions

Cooling towers emissions leave the tower in four streams: evaporation, drift, blowdown and solid waste. Evaporation is the vapor stream from the cooling tower and it predominantly contains air and water. If volatile compounds (from degraded water) are present in the make-up water, they will also be found in the cooling tower evaporation stream. Under certain conditions, fogging can occur on cold days with partial condensation of the water-vapor stream occurring just above the cooling tower. Evaporation also contains trace levels of the chemical constituents found in circulating water from evaporated drift. Depending on ambient conditions, drift should completely evaporate shortly after it exits the cooling tower. Drift is considered as contributory to PM_{10} (mean droplet diameter of 10 microns or less) by many air quality districts. After the

drift has completely evaporated, its constituents would be in the form of particulate matter (e.g. mineral salts and heavy metal salts), condensed/crystallized non-volatile organic compounds and non-aqueous vapor (e.g. volatile organic compounds and ammonia). The chemical constituents found in circulating water exit the cooling tower as a liquid stream in the form of un-evaporated drift and blowdown. Lastly, solid wastes are generated by the cooling tower in the form of sludge that settles in the cold water basin (removed during cooling tower maintenance) and process wastes associated with cooling tower treatment (e.g. side-stream softening). For example, a typical maintenance waste consists of silt from the occasional cleaning of the cooling tower basin. Process sludge can be generated by make-up or side-stream softeners or by side-stream filters. Environmental impacts associated with these emissions are discussed later in Section 4.0, Environmental Impacts.

2.3 Chemical Constituents of Concern in Cooling Water

Cooling tower make-up water typically contains soluble minerals, low concentrations of organic compounds (type and level depends on water source), some biological activity (degree depends on the water source) and suspended solids. The vast majority of cooling towers utilize freshwater for make-up. What separates degraded water from freshwater for cooling tower make-up, other than the source of water, are certain key chemical constituents. These constituents control the allowable operating chemical concentration of the cooling tower, and thus, water consumption and wastewater generation. As stated previously, there are some cooling systems that are successfully utilizing treated municipal effluent. In some instances, depending on constituents, degraded water may be suitable for cooling tower make-up with minimal or no treatment.

2.3.1 Types of Degraded Water

Degraded water can be defined by many parameters, but for the purposes of this paper, it is described as non potable, i.e. groundwater or surface water impacted by naturally-occurring minerals or human impacts and wastewater generated by human, industrial or agricultural activities. Some degraded water examples follow:

- Contaminated surface water or groundwater that contains volatile- or non-volatile organic compounds, pesticides, heavy metals, etc.
- Surface water or groundwater impacted by agricultural activities, e.g. irrigation or livestock operations
- Naturally occurring brackish water deemed too salty for human consumption or irrigation
- Treated municipal effluent (reclaimed water)
- Produced water from oil-field operations

Refer to Table 2-2 for categories of degraded water that will be addressed in this report. Table 2-2 was developed because regulatory agencies in California do not map the extent of, categorize or locate degraded water sources. General data can be gathered from NPDES permit (the

National Pollution Discharge Elimination System is discussed further in Section 2.4, Rules and Regulations) permit files on the type of discharge, approximate daily volume of discharge, and waste category (no specific chemical constituent data are required). There is no centralized data gathering system for degraded groundwater. Each of the nine Regional Water Quality Control Boards as well as the Department of Health Services maintains their own files (in their own formats). The data are usually generated by companies or individuals who have consented to assess the extent of contamination of groundwater (and sometimes surface water). The chemical data is only specific to the type of contamination, e.g. volatile organic compounds and kindred products found in gasoline. As such, the data is not complete enough for evaluating a contaminated source as cooling tower make-up water. Therefore, candidate degraded groundwater sites usually require a full mineral analysis as well as data relating to the nature of contamination. Refer to Table 2-1 for the types of chemical constituent data required to assess degraded water for cooling water.

2.3.2 Chemical Species Typically Found in Degraded Water

Aside from the significant regulatory issues relating to polluted waters (refer to Section 2.4, Environmental Rules and Regulations), the cooling system is sensitive to certain mineral salts which are typically not associated with degraded water (as defined above), e.g. calcium, magnesium, alkalinity, chloride, sulfate, silica, etc. Again, refer to Table 2-1. Degraded water sources sometimes contain chemical constituents of concern not found in freshwater, e.g. phosphate and ammonia. Many constituents of concern, which by definition create degraded water, are not constituents of concern in cooling systems. For example, trace levels of volatile organic compounds do not interfere with cooling tower operation. To summarize, the types of constituents that effect cooling tower operation fall into two groups:

- General mineral constituents which directly effect cooling tower operation (via scale formation, corrosion, fouling, etc.), e.g. calcium, magnesium, alkalinity, sulfate, silica, etc. General mineral constituents are found in all water sources whether fresh or degraded.
- Constituents that are regulated and also effect cooling tower operation, e.g. copper, sulfide, ammonia, phosphate, BOD, etc.

Many regulated constituents do not impact (physically or by way of corrosion) cooling tower operation, e.g. volatile organic compounds, pesticides, some heavy metals, etc. Also, regulatory requirements provide controls for many constituents in degraded waters, e.g. air quality regulations will require the treatment of degraded water for volatile or semi-volatile organic compounds before its used for cooling. There are probably a number of regulated constituents in degraded water that will impact cooling tower operation and have not been identified as yet.

Lastly, cooling tower and cooling loop environments promote biological activity:

- Warm circulating water
- Aerobic environments in open and circulating sections and anaerobic environments in quiescent areas (low flow zones)

- Cooling tower packing/film, heat-exchanger surfaces and silt/debris provide surfaces to establish colonies
- Airborne and waterborne nutrients
- Degraded water constituents such as BOD, ammonia and organic compounds
- Wet/dry interface in film fill

2.3.3 Impacts of Chemical Constituents on Water Consumption, Source Selection and Waste Generation

Refer again to Figure 2-1, Source Water Evaluation methodology. In assessing proposed water sources, *constituents of concern must be evaluated*. Any one constituent could eliminate a possible source or require the imposition of significant treatment. Cooling tower chemistry criteria are used to evaluate constituents of concern. Refer to Table 2-1 for a list of constituents of concern. Note, that some of the criteria in Table 2-1 can be considered key parameters for degraded water, i.e. PO_4 (total phosphate), Cu (copper), Al (aluminum), S (sulfide), NH_3 (ammonia), BOD (biological oxygen demand) and COD (chemical oxygen demand). There also may be other chemical constituents that are specific to degraded water that have not been identified yet.

The last criteria cited in Table 2-1 are the Langelier Saturation (LSI), Ryznar Stability (RSI) and Puckorius Scaling Indices (PSI). The LSI was developed over 60 years ago to predict scaling and corrosion tendencies in water distribution systems. Later these indices were adopted to evaluate cooling water. The LSI evaluates key variables (calcium hardness, alkalinity, temperature and TDS) and determines pH_s - the pH of CaCO_3 saturation. If the difference between the actual pH of the source water and pH_s ($\text{pH} - \text{pH}_s$) is positive, the water has a scaling tendency, i.e. calcium carbonate is above its saturation level and will likely precipitate. A negative difference predicts no calcium carbonate scaling and the water will likely create a corrosive condition for mild steel pipe (in the absence of saturation, the pipe surface has no protective layer of CaCO_3 and is directly exposed to corrosive agents such as oxygen). An ideal range for LSI is 0 to 1. The RSI (a variation on the LSI calculation) was developed to more closely predict calcium carbonate scaling and corrosion. RSI was developed by correlating empirical data based on actual municipal water systems. If RSI is greater than 7, corrosion is likely, and if it less than 6, scaling is likely. An ideal range for RSI is 6 to 7. The PSI modifies the Ryznar Index by calculating the system pH instead of using actual pH. The calculated pH reflects the actual alkalinity of the water and more accurately predicts scaling tendencies, especially in low-alkalinity waters. Note, these indices only predict tendencies of the bulk fluid in a cooling system and should only be limited to this level of analysis. Refer to Table B-1 in Appendix B for LSI, RSI and PSI calculation procedures.

2.3.3.a Cycles of Concentration

Cycles of concentration, N, as described earlier, refers to the multiple of the concentration of a chemical constituent as a result of cooling tower evaporation (as water evaporates the salts stay

behind and concentrate). The “cycled” concentration of a given constituent can be calculated by multiplying make-up concentration by N. Cooling tower blowdown, the wastewater stream from the cooling tower, is utilized to control concentration. Blowdown is usually withdrawn from the hot-water return to the cooling tower. However, depending on the particular configuration of the cooling loop, blowdown can be withdrawn from a number of points in the system (hot or cold side). The make-up or feed rate to the cooling tower is adjusted to compensate for losses from evaporation, drift (usually a very small volume of cooling water) and blowdown. N is calculated by the following flow and mass balances:

$$MU = E + BD + D \quad (\text{flow balance}) \quad (3)$$

where: MU make-up rate, gpm
 E Evaporation rate, gpm
 BD Blowdown rate, gpm
 D Drift rate, gpm

$$MU \times C_{MU,i} = E \times C_{E,i} + BD \times C_{BD,i} + D \times C_{D,i} \quad (\text{mass balance}) \quad (4)$$

where: $C_{BD,i}$ Concentration of chemical constituent “i” in the circulating water

$$C_{E,i} = 0 \quad (\text{evaporation only consists of water vapor}) \quad (5)$$

$$C_{D,i} = C_{BD,i}, \quad (\text{drift is comprised of circulating water}) \quad (6)$$

Substituting (5) and (6) into (4) yields:

$$MU \times C_{MU,i} = C_{BD,i} \times (BD + D) \quad (7)$$

$$N_i = \frac{C_{BD,i}}{C_{MU,i}} \quad (8)$$

where: N_i Cycles of concentration of constituent “i”

Substituting (8) into (2) and (7) and solving for BD yields:

$$BD = \frac{E}{N - 1} - D \quad (9)$$

For each chemical constituent of concern in a degraded water source, there will be a maximum allowable cycles of concentration. Calculating N is critical, since it not only establishes operating concentrations of key constituents, it also establishes flow conditions for the cooling system. Staying below that value will minimize scale and/or corrosion in the cooling loop. After the proposed water sources have been fully characterized on a flow capability and chemical basis, cooling tower chemistry criteria found in Table 2-1 should be imposed to evaluate the

maximum N value for each constituent of concern. Regulatory criteria may also apply, e.g. the RWQCB may impose a limit on certain constituents such as copper or ammonia to meet their Water Quality Objectives for the point of discharge (discussed later in Section 2.4, Environmental Rules and Regulations). The output of this analysis will be the maximum cycles of concentration - chemistry-driven or regulatory-driven - achievable without treatment for each source of water. Note again, the smallest value of N for the suite of chemicals of concern defines the design cycles of concentration for a given source of water.

Blowdown is calculated based on cycles of concentration (Equation 9 above) - the smaller the value of N, the larger the blowdown rate. Refer to Figure 2-4. Note that below 4.5 to 5.5 cycles of concentration, blowdown rates increase dramatically. Depending on water availability and discharge limitations, large volumes of blowdown may not be feasible regardless of source water quality. This is especially true for projects sited in desert or Central Valley locations where all wastewater is typically “contained” via discharge to lined evaporation ponds. Many projects in these locations are forced to evaluate treatment options (for freshwater as well as degraded water) that allow high cycles of concentration.

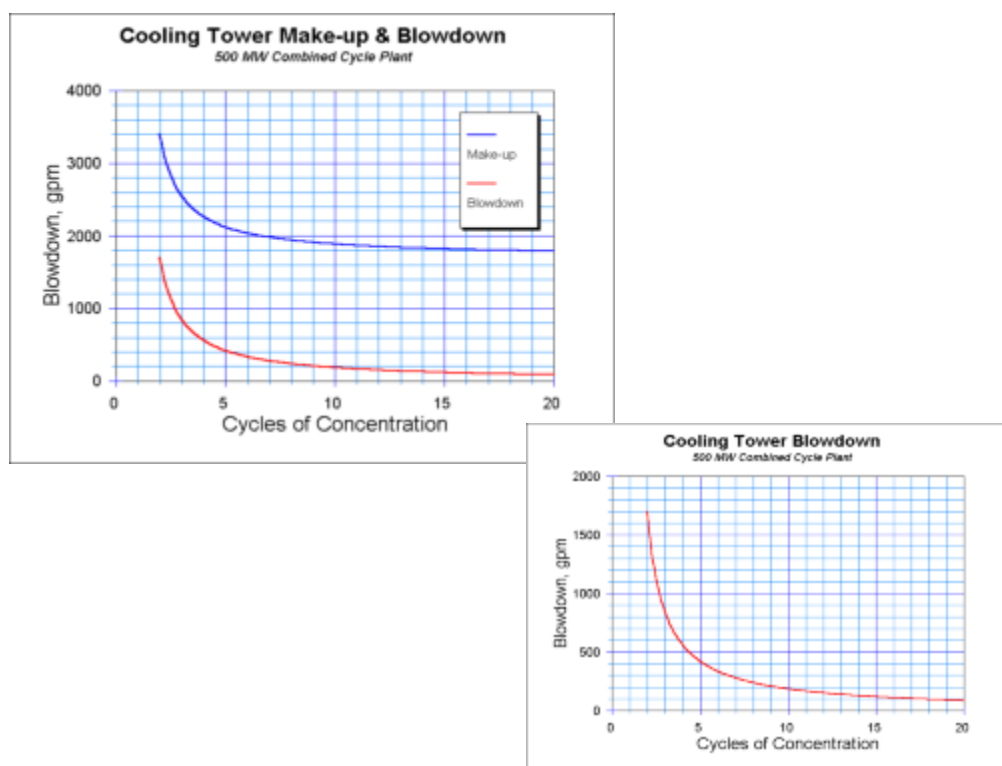


Figure 2-4
Make-up and Blowdown vs Cycles of Consentration

2.3.3.b Water Quality Criteria Prediction Software

Reference is made to SEQUIL RS in Table 2-1 for many of the criteria. Some of the criteria in the table are defined by a simple limit, while some have no identified limit. EPRI developed WinSEQUIL (EPRI, 1999) software to address the complexity of cooling system chemistry which cannot be represented by simple rules of thumb. The focus of the software in this first phase of development (further development is currently not planned) was to help the user identify operating scenarios that will likely result in scale formation. Generally, scale-forming constituents specific to a source water can interact to form non-precipitating ionic associations, thereby increasing their apparent solubility and allowing for higher cycles of concentration.

Also, salts are more soluble at higher TDS levels. The software predicts saturation levels of 11 precipitating salts, 43 soluble ionic associations and 3 soluble gas relationships for a given source water chemistry. The software does not calculate maximum cycles of concentration. The evaluator must calculate an assumed chemistry at different cycles of concentration, elect whether to include atmospheric interactions with certain dissolved gases and assume an operating pH (there are other selections as well). Overall, the software requires a basic understanding of reaction chemistry and multi-phase equilibrium relationships to be fully used and appreciated.

Of significance, no allowance is made for specialty chemicals in SEQUIL RS (this was to be accomplished in a later phase of development). Even with ionic associations that allow higher cycles of concentration, specialty chemicals permit operating conditions in excess of saturation. Many specialty chemical programs are multi-functional and involve scale control, dispersion of scale products and corrosion protection. There are commercial software packages that assess ionic associations, calculate the saturation of scale-forming salts at different cycles of concentration and take into account specialty chemical solubility enhancements.

If software is not used in evaluating source water, the criteria found in Tables 2-3 and 2-4, which are conservative and therefore somewhat safe, can be used to evaluate the impact of chemical constituents found in the source waters. The criteria are also summarized below:

- Calcium and alkalinity - utilize the 1982 EPRI criteria.
- Sulfate - utilize the CaSO_4 solubility product. The CaSO_4 product can also be used for determining the calcium limit.
- Phosphate - ortho-phosphate (expressed as PO_4^{-3}) which represents a very small fraction of the total phosphate concentration in a cooling system reacts readily with calcium to form tri-calcium phosphate. $\text{Ca}_3(\text{PO}_4)_2$ is a tenacious scale and its formation is very sensitive to pH. If phosphate is present, assume that the pH of the circulating water will have to be strictly held in the range of 6.8 to 7.2. The higher the TDS of the source water the greater solubility of tri-calcium phosphate. Refer to Table 2-4 for maximum calcium levels as they relate to circulating water pH and TDS. The phosphate concentrations in Table 2-4 are at saturation, i.e. just at the point of precipitation. There are scale inhibitors and dispersants currently on the market that allow phosphate concentrations at significantly higher levels, i.e. two to four times the calcium and phosphate levels in Table 2-4. Assume that a scale inhibitor and/or

dispersant will be required. Before finalizing cooling parameters for phosphate, consult with a specialty chemical provider.

- BOD and COD - there are no criteria for these types of constituents, however, the less the better (less than 100 mg/l in the circulating water) since these parameters encourage biological activity and increase the demand for biological control chemicals, e.g. chlorination.

2.3.3.c Water Supply Screening

Screening involves comparing cycles-of-concentration constraints (based on chemical criteria), make-up water demand and blowdown for the water sources being evaluated. Screening is used to identify the specific chemical constraint(s) that limit cycles of concentration, and thus, possibly eliminate a water source from further consideration or identify the need for pretreatment. Refer to Table 2-5 for a comparison of four actual sources of degraded water and freshwater. The produced water, agricultural return water and freshwater sources in the table are located in the Central Valley of California and the reclaimed water source in the Bay Area. Each source was evaluated based on the chemical criteria found in Table 2-1.

Note, a regulatory analysis (wastewater quality and generation) was not performed in this specific evaluation, e.g. identification of organic compounds, heavy metals, etc. Regulatory concerns (see section 2.4, Environmental Rules and Regulations) should be considered in the screening of degraded water sources, especially when regulatory red flags are encountered, e.g. contaminated groundwater with high levels of MTBE.

Given the pressures associated with water use in California, there will be competition for other uses of treated contaminated groundwater, especially if its is a drinking water resource. Likely, the same or similar remediation treatment requirements for the removal of organic compounds, pesticides or heavy metals will also apply to water used for cooling tower make-up. Again, refer to Section 2.4.

Before the screening analysis was conducted, the sulfuric acid requirement for cooling tower pH and alkalinity control was estimated. Sulfuric acid is added to make-up water to control cooling water alkalinity and pH. Refer to Tables 2-3 and 2-4 as well as Table B-2 in Appendix B for control criteria and cycles-of-concentration formulas. Sulfate concentrations can significantly increase in cooling tower feed water as a result of acid addition especially in highly alkaline source waters. For screening purposes, acid addition was based on five cycles of concentration. This estimating approach is adequate for screening. However, if more accuracy is desired, the sulfate-addition calculation can be repeated (using the newly calculated value for cycles of concentration as a basis for acid addition) until the iterated value changes minimally.

As expected, freshwater fared well in this analysis. It had a silica limitation of 9.4 cycles of concentration. After a source water is selected, a detailed evaluation would be conducted which would require iterative/multiple adjustments to operating assumptions.

Table 2-3
Cooling Tower - Basic Water Quality Parameters

Parameter	Units	Basic Parameters	
Ca	mg/l _{CaCO3}	900 (max) ₍₅₎	
Ca x SO ₄	(mg/l) ²	500,000	
Ca with PO ₄ present	mg/l _{CaCO3}	(Refer to Table 2-3b)	
Mg x SiO ₂	mg/l _{CaCO3} x mg/l _{SiO2}	35,000 ₍₂₎	75,000 ₍₃₎
HCO ₃ + CO ₃	mg/l _{CaCO3}	30-50 ₍₂₎	200-250 ₍₃₎
SO ₄	mg/l	(Note 5)	
SiO ₂	mg/l	150	
Fe (Total)	mg/l	<0.5	
Mn	mg/l	<0.5	
Cu	mg/l	<0.1	
Al	mg/l	<1	
S	mg/l	5	
NH ₃	mg/l	<2 ₍₉₎	
pH		6.8-7.2 ₍₂₎	7.8-8.4 ₍₃₎
pH with PO ₄ present		7.0-7.5 ₍₄₎	
TDS	mg/l	70,000	
TSS	mg/l	<100 ₍₆₎ - <300 ₍₇₎	
BOD	mg/l	<100 ₍₄₎	
COD	mg/l	<100 ₍₄₎	
Langelier SI ₍₈₎		<0	
Rysnar SI ₍₈₎		>6	

Notes.....

1. Cooling tower circulating water concentrations. PO₄ refers to total phosphate concentration. Refer to Table 3-1 and for detailed calculation pocedures.
2. Without scale inhibitor.
3. Assumes scale inhibitor is present.
4. Consult with specialty chemical provider before finalizing control parameters.
5. Refer to the CaSO₄ limit.
6. <100 mg/l TSS with film fill.
7. <300 mg/l TSS with open fill.
8. Refer to Appendix A for a discussion of the Langelier and Ryznar Saturation Indices for calcium carbonate.
9. <2 mg/l NH₃ applies when copper bearing alloys are present in the cooling system. This does not apply to 70-30 or 90-10 copper nickel.

Table 2-4
Maximum Cooling Tower Calcium with PO₄ Present

pH	PO ₄ mg/l	Max Ca, mg/l CaCO ₃ @ Cooling Tower TDS, mg/l				
		500	2,500	5,000	10,000	20,000
7.00	5	110	160	200	250	285
7.25	5	70	100	130	165	190
7.50	5	40	65	85	105	125
7.00	10	70	100	125	160	180
7.25	10	45	65	80	105	120
7.50	10	25	40	50	65	80
7.00	15	55	75	95	120	140
7.25	15	35	50	60	80	90
7.50	15	20	30	40	50	60

Notes.....

1. Cooling tower circulating water concentrations. PO₄ refers to total phosphate concentration. Refer to Table 3-1 and for detailed calculation pcedures.
2. Assumes scale inhibitor is present.
3. Consult with specialty chemical provider before finalizing control parameters.

Table 2-5
Source Water Screening

	Produced Water mg/l	Ag Return Water mg/l	Reclaimed Water mg/l	Fresh Water mg/l
Na (by difference)	982	2,182	76	41
K	22	6	5	0.72
Ca	40	554	76	18
Mg	13	270	43	0.76
HCO ₃	1,100	239	396	92
Cl	920	1,480	102	22
SO ₄	110	4,730	68	31
NO ₃	NR ⁽⁶⁾	48	NR	ND
Total PO ₄	NR	2	6	ND
S	6	NR	NR	ND
SiO ₂	120	37	17	16
B ⁽⁵⁾	21	14	3	0.17
NH ₃	5	NR	5	ND
TDS	3,879	9,723	869	297
TSS	<1	11	8	<1
BOD	30	3	8	NA
COD	80	32	5	NA

Operating Cooling Tower Assumptions.....

Cooling Tower Alkalinity, mg/l CaCO ₃	200	50	50	200
Calculated pH ⁽⁸⁾	7.9	7.0	7.0	7.9

Screening-Level Cycles of Concentration - N - without Pre-Treatment

(Refer to Tables 2-3a and 3b for control criteria and Table B-2 for calculation procedures)

Ca	9.0	<1	4.7	20.0
Ca x SO ₄ ⁽⁷⁾	3.6	<1	4.2	16.4
Mg x SiO ₂	3.4	1.3	5.0	38.7
SiO ₂	1.3	4.1	8.8	9.4
Ca (in presence of PO ₄)	NA	<1	1.3	NA
TDS	18	7	80	235

Notes.....

1. Produced water from oil production in the Central Valley.
2. Agricultural return water from the San Luis Drain.
3. Secondary-treated reclaimed water from the Bay Area. t-PO₄, B, NH₃ and COD were estimated.
4. West Kern water. Silica concentration was modified for this analysis.
5. B exists as H₃BO₃ (non-dissociated boric acid) in water at this pH.
6. NR = not reported, ND = non-detectable and NA = not applicable.
7. H₂SO₄ used for pH control is accounted for when calculating the impact of additional SO₄ on CaSO₄ solubility.
8. Assume pH = 7.0 when PO₄ present.

Reclaimed water would have been limited to 4.4 cycles of concentration based upon calcium sulfate criteria, however, the phosphate concentration is very high. In addition, produced water and agricultural return water had problems with calcium, calcium sulfate, magnesium/silica and silica. Note that phosphate posed problems for both agricultural return water and reclaimed water. Unless treated, these criteria severely limit the achievable cycles of concentration rendering the water unusable.

Ammonia concentrations can be quite high (20 to 50 mg/l) in reclaimed water. If copper alloys are present in the cooling system (e.g. admiralty brass), the ammonia limit of 2 mg/l must be applied to prevent severe corrosion (refer to Table 2-1). This limit does not pertain to copper-nickel alloys (90-10 and 70-30) which are sometimes used for condenser tubing. Note, copper corrosion as a result of exposure to ammonia could create an environmental discharge problem in the form of soluble and complex copper species. Ammonia in the circulating water will create the need for significant copper protection, e.g. a copper-specific corrosion inhibitor such as tolyltriazole. One alternative to specialty chemicals is the elimination of copper alloys (with the exception of copper-nickel alloys) in a planned cooling system. This applies to all wetted surfaces. 70-30 copper-nickel, 90-10 copper-nickel, 316 stainless steel or titanium are common alternatives to copper alloys for heat exchangers, e.g. the main condenser, auxiliary coolers, etc. Depending on the municipal wastewater treatment plant, nitrification could be employed to convert ammonia to nitrate and essentially eliminate it from the cooling tower make-up stream (most municipal plants do not employ nitrification). Lastly, NH_3 and NH_4^+ promotes biological growth and is metabolized by biological activity in the cooling system (nitrification). Ammonia is also consumed by oxidation during routine system chlorination to form chloramines (approximately 10 mg/l of chlorine for every mg/l of ammonia). Chloramines, which are not nearly as potent as chlorine, are long-lived, so they provide some level of residual biological control. Conversely, persistent chloramine residuals could also exceed regulatory requirements for total residual chlorine in cooling tower blowdown (discussed later - refer to Table 2-9). Bromine and chlorine dioxide (ClO_2) can be used in the presence of ammonia. Bromine reacts with ammonia but the reaction product is unstable and reverts to OBr^- . Also, bromine is more reactive in alkaline water (pH greater than 7.5) than OCl^- . Chlorine dioxide does not react with ammonia. Both biological control chemicals are more costly than sodium hypochlorite.

Lastly, Alloy selection should be performed carefully. The metallurgical guidelines discussed above should be considered “starting points”. Metallurgy selection should be conducted on a case-by-case basis.

Long-term water usage should be taken into consideration when screening source waters for cooling tower make-up. Freshwater that is available today may not be available in the future.

2.3.3.d Treatment Requirements for Degraded Water

As can be seen in the screening analysis presented in Table 2-5, cycles of concentration may be significantly limited by one or more constituents for each degraded water source. For source waters that are impacted by scale, corrosion or environmental factors, there are commercially available treatment technologies that can be employed. Refer to Figure 2-5. Treatment generally falls into three categories, and depending on site-specific requirements, one, two or all three of the categories could be employed for a degraded water source. Each category has a general purpose. Pre-treatment can be utilized to remove contaminants, adjust pH, soften (remove calcium and magnesium), reduce silica or reduce TSS. Side-stream can be used to soften, reduce silica or reduce TSS. Lastly, post treatment is utilized to reduce blowdown volume or meet discharge requirements. These categories are discussed in Sections 3 and 5.

As depicted in Figure 2-5, specialty chemicals are integral to cooling tower operation and cooling water treatment. These chemicals are used to minimize corrosion and scale as well as enhance treatment process performance for many technologies (also discussed in Section 3, Identify Technical and Economic Feasibility of Using Degraded Water for Cooling Towers).

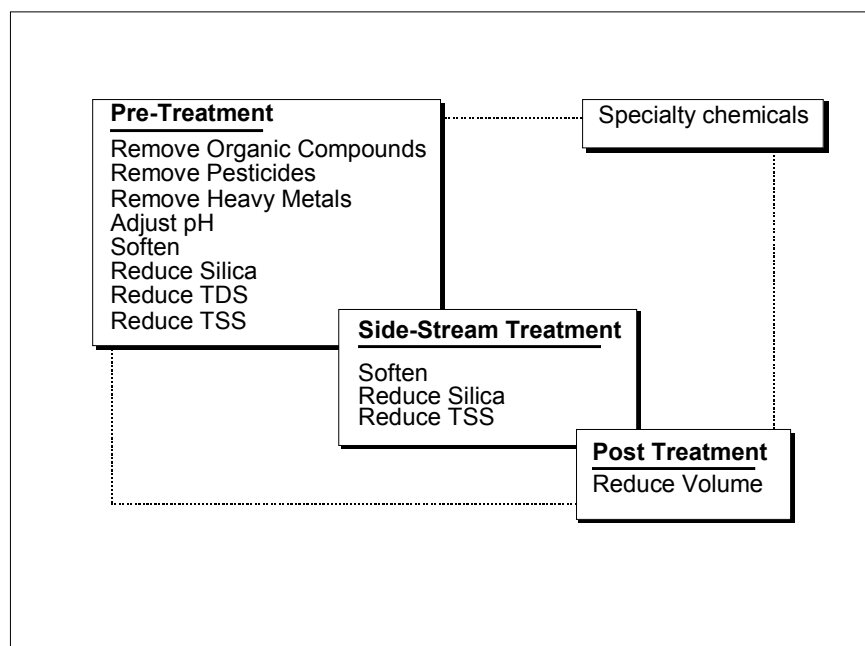


Figure 2-5
Cooling Water Treatment

Tables 2-6 and 2-7 summarize treatment requirements for degraded water (treatment is often used for freshwater sources as well). The treatment requirements in Table 2-7 are typical strategies employed for contaminated groundwater. Treatment technologies will be discussed in depth in Sections 3 and 5.

Treatment requirements for each degraded water example identified in Table 2-5 are briefly discussed as follows:

Produced water is limited by calcium sulfate, magnesium/silica and silica. Magnesium is relatively low but the silica concentration is quite high, which is typical for this type of water. Silica reduction is best achieved with side-stream warm lime or lime/soda softening (technology discussed in Sections 3 and 5) - this water is typically pulled from the condenser return to the cooling tower (hot side). Warm softening significantly enhances silica removal. Also, note that bicarbonate alkalinity is very high and a significant amount of sulfuric acid will be required to reduce feedwater alkalinity for pH control. Lastly, ammonia levels will necessitate the use of non-copper bearing alloys in the cooling system.

Agricultural return water is severely limited by calcium, calcium sulfate, magnesium/silica and calcium phosphate. All constituents are treatable with softening. Side-stream lime/soda softening will be required to remove silica effectively. Bicarbonate alkalinity is very high and a significant amount of sulfuric acid will be required to reduce feedwater alkalinity for pH control. Calcium, magnesium and phosphate will also be reduced by this type of softening.

Reclaimed water is limited by calcium, calcium sulfate and calcium phosphate - 4.4 to 4.7 cycles of concentration. All of these limitations could be controlled with calcium removal via make-up or side-stream softening. Note, ammonia levels are very high, and as with produced water, will necessitate the use of non-copper bearing alloys in the cooling system. Bromine will also be required in lieu of chlorine to avoid chloramine formation (again, discussed Section 4).

Refer to Table 2-7 to review treatment requirements to treat a variety of environmental contaminants typically found in groundwater and surface water. These are common treatment technologies employed to remediate contamination. Treated water chemistry, chemical requirements, treatment technology and overall economics are discussed in detail in Sections 3 and 5.

Table 2-6
Pre-, Side-Stream Treatment for Cooling Towers

Cooling Tower Chemical Criteria (Note 3)	<i>Pre-Treatment</i>		<i>Side-Stream Treatment</i>	
	pH Adjustment	Lime or Lime/Soda Softening	Filtration	Warm Lime or Lime/Soda Softening
Ca		Pri		Pri
Ca x SO ₄		Pri via Ca		Pri via Ca
Mg x SiO ₂		Pri via Mg		Pri
M Alkalinity	Pri	Sec		Sec
SO ₄		Pri via Ca		Pri via Ca
SiO ₂		(Note 5)		Pri
PO ₄		Sec		Sec
pH	Pri			
TSS		Sec	Pri	Sec

Notes.....

1. Pri = primary means of reduction - intention of process.
2. Sec = secondary means - incidental reduction in process.
3. Chemical criteria found in Table 2-1.
4. Refer to Table 2-6 for removal of contaminants from degraded water for cooling tower make-up.
5. There is some removal of SiO₂.

Table 2-7
Pre-Treatment of Contaminated Water for Cooling Tower Make-Up

Chemical Parameter (Note 5)	Air Stripping Vapor-Phase GAC (Note 3)	Air Stripping Vapor-Phase Thermal Oxidation	Liquid Phase GAC	Biological Treatment (Note 4)	Strong Base IX	Chelating IX	Precipitation Co-Precip
Organic Compounds	Pri - Volatile	Pri - Volatile	Pri	Pri	Sec		
Pesticides			Pri	Pri (8)	Sec		
Cationic Heavy Metals (12)						Pri	Pri
Anionic Heavy Metals (13)				Pri (14)	Pri		Pri (11)
NO ₃ , ClO ₄ , F (9)				Pri - NO ₃ , ClO ₄	Pri (10)		
Biological (6)			Sec (7)	Pri	Sec		

Notes.....

1. Pri = primary means of reduction - intention of process
2. Sec = secondary means - incidental reduction in process
3. GAC is granular activated carbon.
4. There are a variety of biological processes, e.g. constructed wetlands, trickling filter, fixed-film aerobic, etc.
5. Refer to Table 2-2 for chemical parameters of contaminated groundwater and surface water treatment.
6. Biological waste components include BOD, COD, NH₃, PO₄, etc. Typically found in reclaimed water as well as pharmaceutical, biotech, livestock/dairy and food processing waste streams.
7. There will be some incidental removal of BOD and COD.
8. Pesticides could be detrimental to biological processes because of its toxicity.
9. Anaerobic biological treatment is required for NO₃ and ClO₄. Anaerobic treatment is still considered experimental for ClO₄.
10. Depending on treatment conditions NO₃ removal may not be completely achievable.
11. Applies to AsO₄ and SeO₃.
12. Cationic heavy metals include Cu, Ni, Cd, Cr (+3), etc.
13. Anionic heavy metals include AsO₄, CrO₄, SeO₄, SeO₃, etc.
14. Anaerobic biologic treatment is still somewhat experimental for anionic heavy metals.

2.3.3.e Post-Treatment Requirements for Degraded Water

Most planned and many existing inland power plants in California will be designed as “zero discharge”, i.e. all wastewater is contained. Depending on the water source and the achievable cycles of concentration, wastewater generation in the form of cooling tower blowdown can be quite high (usually the largest waste stream at the plant). Wastewater in desert settings is often routed to imperviously-lined evaporation ponds for final on-site disposal. The focus of post treatment is to treat blowdown to reduce wastewater generation. Also note, in zero discharge plants, many waste streams are routed to the cooling tower, e.g. HRSG blowdown, plant washdown, ion exchange low-conductivity rinse water, etc. Sanitary wastewater is usually handled separately.

Volume reduction is costly and almost always requires a combination of softening, evaporation or crystallization. A benefit of wastewater treatment via evaporative processes is a significant amount of high quality water is generated which can be reused in the plant, e.g. HRSG feedwater, inlet air cooling for the gas turbine, NO_x control, etc. These technologies will be discussed in Sections 3 and 5.

2.4 Rules and Regulations

The environmental impacts of a variety of cooling systems (once through, wet cooling, etc.) have been the object of legislative and regulatory attention at both the Federal and State level. The regulatory framework and specific rules, which apply to steam-electric power plant cooling in California, will be reviewed in the following section. The discussion will be confined to wet evaporative cooling with particular emphasis on those elements which would be most affected by the use of degraded water for cooling tower make-up.

Environmental issues related to new power projects are numerous and complex. The following information is presented in a generalized manner and is intended to identify issues of concern rather than specific regulatory requirements.

2.4.1 Regulatory Background and Approach

Cooling system impacts may involve all the environmental media (air, water and land) and potential impacts to public health. Therefore, they are governed by many parts of environmental laws and regulations. At the Federal level, these include the Clean Air Act, the Clean Water Act, the Resource Conservation and Recovery Act, and resultant regulations promulgated under NPDES, National Emissions Standards for Hazardous Air Pollutants (NESHAPS) and others. At the state level, relevant rules are found in the California Code of Regulations, especially Titles 17, 20, 23, 26 and 27 (Public Health, Public Utilities and Energy, Waters, Toxics and Environmental Protection respectively) and policies established by the State and Regional Water Quality Control Boards. *Refer to Appendix A.1.1, Referenced Citations - Chapters 1 and 2 (citations 11 through 23) for a comprehensive list of related statutes discussed in this section.*

In past years in the federal framework, the regulatory philosophy was based on the requirement that responsible facilities mitigate environmental impacts with the most effective control technology applicable to their particular situation. Hence for steam-electric power generation, Clean Water Act Technology-based limits are categorized (generally based on the age of the plant) as follows:

- BPT - Best Practical Control Technology Currently Available - note, since the early 1980s, the only aspect of BPT that applies to any current or future discharges is pH limits of 6.0 - 9.0. Other BPT controls are superseded by BAT.
- BAT - Best Available Technology Economically Achievable
- NSPS - New Source Performance Standards (for new power plants)
- PSES- Pretreatment Standards for Existing Sources - pretreatment standards for discharge to sanitary sewer.
- PSNS - Pretreatment Standards for New Sources - pretreatment standards for discharge to sanitary sewer.

The cost which the operator might be required to bear is given consideration depending on the perceived severity of the impact.

More recently at the state level, the regulatory philosophy has shifted to consideration of goals and objectives for the state's environment as determined by the intended use of the particular affected receiving body (e.g. swimming, fishing, domestic use, industrial use, etc) and its current condition. Effluent limitations or control technology requirements are then set on a case-by-case basis as necessary to achieve the desired goals and objectives.

2.4.2 Statutory Basis for Regulations

The rules governing the use and discharge of water from power generation in California are established in three regulatory areas:

- Policy promulgated by the California State Water Resources Board, specifically under Resolution #75-58, in effect since 1975.
- Federal rules pursuant to CFR Title 40: Environmental Protection including the Clean Water Act and the NPDES permitting requirements;
- The recently adopted State Implementation Plan and the California Toxics Rule.

To discuss the interrelated elements of the rules and regulations, the following sections are introduced and organized based on the "Information Requirements for Application" to obtain CEC approval for proposed power plants (greater than 50 MW). Table 2.7 summarizes all the specific references to power plant cooling systems and identifies the regulations and code citations relevant to each aspect of the environmental impact.

2.4.3 Regulated Discharges and Impacts

The following subsections will review the major environmental issues related to power plant cooling and the relevant rules and regulations as follows:

- Water consumption
- Waste water discharge
- Drift (air quality regulations)
- Toxic emissions
- Noise
- Visual resources

2.4.3.1 Water Consumption

Much of the information required by Title 20 under Power Plant Cooling System Requirements for Approval (refer to Table 2-8) is intended to address the appropriateness of using water for power production in light of other needs in California, e.g. domestic consumption. The regulatory philosophy is based on policy promulgated by the California State Water Resources Board in their Resolution No. 75-58, Water Quality Control Policy on the Use and Disposal of Inland Waters Used for Power Plant Cooling. It is intended to guide the actions of the State and Regional Water Regional Control Boards and to establish the following principles:

- Protecting beneficial uses of the state's water resources and
- Keeping the consumptive use of freshwater for power plant cooling to that minimally essential for the welfare of the citizens of the state.

The Policy addresses both water withdrawal for use and the discharge of waste water from the cooling systems. Specific elements of the Policy include:

- Power plant cooling water should come from the following sources in the following priority of order:
 - Wastewater being discharged to the ocean
 - The ocean
 - Brackish water from natural sources or irrigation return flow
 - Inland wastewaters of low TDS
 - Other inland waters
- Fresh inland waters will be used only when it is demonstrated that other sources or other methods are “environmentally undesirable or economically unsound.” (Note, emphasis added in original text.) No quantitative guidance is provided for these determinations which are left to the exercise of reasonable judgement on a case-by-case basis.
- Analyses of alternative cooling systems employing dry and wet/dry modes of [cooling] operation and of the feasibility of using wastewater are encouraged.

For discharge considerations it should be noted that:

- Discharge of blowdown to land disposal sites is prohibited except to salt sinks or to lined facilities.
- Discharge from once-through inland facilities is prohibited unless existing water quality and aquatic environment is maintained.

Table 2-8
Power Plant Cooling Systems - Requirements for Approval

California Code of Regulations, Title 20, Div. 2, Chap. 5---§2012, App. E

Subsection (of App. B)	Subject	Requirement	Relevant Code/Regulation
(a)(1)(A)	Executive Summary	General description of....water supply, pollution control systems....	None cited
(b)(1)(C)	Project Description	Design, construction, operation of----cooling systems	None cited
(b)(1)(D)	Site/Facility Selection	How selection made and consideration given to env. impacts, water and----	None cited
(f)(1)&(2)	Alternatives	Discussion of other choices and economic/environmental merits	Public Resources Code, Section 25540.6(b)/Policy 75-58
(g)(4)	Noise		None cited
(g)(6)(F)	Visual Resources	Assessment of impact of visible plumes	None cited
(g)(8)(A)	Air Quality	Info necessary for air pollution control district to complete Determination of Compliance	None cited
(g)(9)	Pubic Health		Health and Safety Code, Section 25294.8
(g)(10)	Hazardous Materials Handling		Cal. Code, title 22, §66261.20 et seq. Also, Health and Safety Code, Section 25531.
(g)(12)	Waste Management		Cal. Code, title 22, §66261.20 et seq.
(g)(13)	Biological Resources		Cal. Code, title 20, Sects. 1702 (q) and (v)
(g)(14)	Water Resources		Waste Discharge Requirements; NPDES; Policy 75-58
(g)(15)	Agriculture and Soils	Effect of emissions on surrounding soil-vegetation	None cited

Cooling tower blowdown volume could be significant with the use of untreated degraded water because chemical constituents found in the water will likely limit cycles of concentration. Therefore, environmental rules will impact water usage and treatment and pre-, in-process or post treatment may be required to minimize discharge volumes (or treat to remove specific chemical compounds).

Disposal issues usually revolve around cooling tower blowdown and treatment waste streams. The volume of the waste stream(s) and chemical characteristics define the extent of the disposal issue. The lower the cycles of concentration, the greater the volume of waste. As stated previously, large waste volumes pose significant problem for plants with no convenient or environmentally-acceptable means of liquid disposal. Also, Water Quality Objectives set forth by the local RWQCB may preclude any type of disposal (discussed later in this section). Conversely, a high cycles of concentration waste stream with elevated concentrations of source-water constituents may also pose disposal problems.

As part of the analysis required to determine the appropriateness of water use at any site, a range of reasonable alternatives sites, including a “no project” alternative must be considered in accordance with California Public Resources Code section 25540.6(b). This must include a discussion of site selection criteria, any alternative sites and reasons for choosing the proposed site. In the context of considering water use for power plant cooling, these are important elements in establishing whether alternatives to inland fresh water use are “environmentally undesirable” or “economically unsound.”

2.4.3.2 Wastewater Discharges

The information requirements for the Regional Water Quality Control Board (identified in Table 2-7, Section (g)(14), Water Resources) include a National Pollutant Discharge Elimination System (NPDES) permit and a Waste Discharge Requirements permit.

2.4.3.2.a Federal Regulations

The basis for regulation of wastewater discharges promulgated at the federal level comes primarily from the Clean Water Act (Federal Water Pollution Control Act Amendments of 1972, as amended by Clean Water Act of 1977). Permitting authority is delegated to the states under the National Pollutant Discharge Elimination System (NPDES). The U.S. Environmental Protection Agency sets discharge limits which the states must meet at a minimum (although they may set more stringent limits at their discretion). These limits are set for individual categories of dischargers on the basis of existing treatment technologies, their costs and their applicability to the particular category. The following limits are for the Steam Electric Power Generating Point Source Category in CFR Title 40, Chapter 1, Part 423; 7-1-99 Edition. Refer to Table 2-9. Note that NSPS, PSNS, PSES and BAT waste discharge limitations are very similar and are described jointly in Table 2-9. An additional category, designated as Best Conventional Pollutant Control Technology (BCT), is “reserved” but currently undefined.

2.4.3.2.b California Regulations

In addition, the regulatory philosophy of many jurisdictions, including California, has shifted from technology-based discharge limits for particular categories to case-by-case determination of allowable limits based on the achievement of water quality objectives for particular receiving waters. These are reviewed briefly for the California situation below.

The basis of wastewater discharge regulations promulgated by state regulatory authorities is the California Water Code and specifically, the Porter-Cologne Water Quality Control Act. Authority is given to the State Water Quality Control Board and nine Regional Water Quality Control Boards to “formulate and adopt water quality control plans” which include:

- “establish[ing] such water quality objectives....[to] ensure the reasonable protection of beneficial uses and the prevention of nuisance
- specify[ing] certain conditions or areas where the discharge of waste....will not be permitted”
- prescrib[ing] requirements as to the nature of any proposed discharge”.

It is under these Regional Board Plans, referred to a “basin plans”, that the operative rules for waste and wastewater discharge to both surface and groundwater are set which eventually determine whether power plant cooling systems are “environmentally undesirable or economically unsound”.

Table 2-9
Steam Electric Power Generating Point Source Category, CFR Title 40, Chapter 1, part 423, BAT, NSPS, PSNS and PSES

Pollutant or Pollutant Property	BAT Effluent Limitation	
pH	6 to 9	
Free Available Chlorine (FAC)	0.5 mg/l, maximum concentration 0.2 mg/l, average concentration	
	<i>One Day Maximum (mg/l)</i>	<i>Average of daily values for 30 consecutive days (mg/l)</i>
126 priority pollutants (Table B) (contained in chemicals required for cooling tower maintenance)	No detectable amount	No detectable amount
Chromium, total	0.2	0.2
Zinc, total	1.0	1.0

Basin Plans

A typical set of procedures and guiding principles is reviewed from “A Compilation of Water Quality Goals” developed by the Central Valley Regional Water Quality Control Board, one of the nine regional Boards in California. The “basin plans” are required to:

- Set water quality standards specific to surface and groundwaters in a region.
- Issue waste discharge requirements (permits) to implement those plans.

The boards are charged to protect beneficial uses, defined by the Central Valley Board to include “power generation, as well as domestic, municipal, agricultural and industrial supply, preservation, enhancement of fish, wildlife and other aquatic resources or preserves.” All surface and groundwaters are to be protected as existing or potential sources of municipal and domestic supply unless specifically de-designated. Exclusions apply if total dissolved solids exceed 3000 ppm, or for low (<200 gallons per day) sustainable yield wells, or contaminated and untreatable water.

Objectives set for specific water bodies include toxicity and chemical constituents and, for the Central Valley also include bacteria, dissolved oxygen, pesticides, pH, suspended materials and salinity.

The most important elements of these plans affecting discharge and waste disposal from power plant cooling systems are the toxicity and chemical constituents elements. Under federal rules, the states have been required to adopt criteria for priority pollutants. A plan adopted by California in 1991 was invalidated by the courts in 1994. California was then without a plan until 2000 when the U.S. EPA issued the California Toxics Rule and the SWQCB issued the Policy for Implementation of Toxics Standards. These two documents are now used together by the regional boards to make case-by-case determinations on waste and wastewater discharge and disposal applications.

California Toxics Rule (CTR)

The CTR establishes numeric water quality criteria for priority toxic pollutants. These feed into effluent discharge limitations through a methodology established in the State Implementation Policy. The listed pollutants and their limits are tabulated in Part 131, Water Quality Standards (§131.38(b) beginning on p. 31712 of the Federal Register, May 18, 2000).

Substances relevant to the power plant cooling discharges include chromium (+3, +6), copper, nickel and zinc and trihalomethanes (typically byproducts of oxidative biological control). Also, depending on source water and receiving water quality, additional constituents of concern could be identified. With these are ambient water quality criteria. In many instances the effluent limitations could be held to these levels which are often well below those listed under the Federal Point Source Discharge limits found in Tables 2.8 and 2.9.

A comparison of state and federal rules follows:

<u>Pollutant</u>	<u>CTR (mg/l)</u>	<u>EPA BAT (mg/l)</u>
Zinc	0.12	1.0
Chromium (+3,+6)	0.18, 0.011	0.2 (total)

State Implementation Policy:

Using the CTR as guidance, the regional boards, under the State Implementation Policy carry out four functions.

- Set applicable objectives
- Establish data requirements
- Determine which pollutants require water quality effluent limitations
- Calculate discharge limitations

Applicable criteria and objectives are taken from the CTR or the regional plans with the more stringent applying if they differ. Within the regions, the limits are set for particular water basins with the objectives of protecting aquatic life or human health/beneficial use. Distinctions between fresh and salt waters are made. In addition, distinctions are made between (MUN (municipal/domestic water supply) and non-MUN water bodies. Other designations include REC1 (water contact recreation).

Data needed to make the appropriate calculations are required of the applicant. Quality assurance and representativeness requirements are also established. The essential result is that the limit is set at the ambient water quality criteria in cases where the existing ambient level equals or exceeds the criterion. If the ambient level is less than the criterion, the discharge limit can exceed the criterion by the difference if a dilution credit is granted. The usual result is non-degradation policy which sets very stringent discharge limits.

2.4.3.3 Air Quality Regulations

Air-borne emissions from cooling towers are primarily associated with cooling tower drift. Drift consists of the small droplets of circulating cooling water that are entrained by the air passing through the tower. Drift eliminators keeps these losses to very low levels, and are typically rated from 0.002 to 0.008 percent of the circulating water flow rate (more efficient eliminators are being developed). At a rating of 0.002 percent, the drift rate would be 2.5 gpm for a 500 MW combined cycle plant (approximately one half the flow from a hand-held garden hose). It is has not been clearly demonstrated how much of the drift constitutes PM₁₀ emissions.

2.4.3.3.a Federal Regulations

Air-borne emissions from cooling towers are regulated under the Clean Air Act, specifically the provisions of NESHAPS. Listed pollutants under NESHAPS with relevance to wet cooling towers include asbestos (in the case of older towers using cement-asbestos [CAB] fill), chromium, zinc and zinc oxide, and the tri-halomethanes. Also, Title 40 (Chapter 1, Part 63, NESHAPS for Source Categories, Subpart Q, NESHAPS for Industrial Process Cooling Towers (IPCT), Section 63.402) states:

“No owner....shall use chromium-based water treatment chemicals in any affected IPCT.”

2.4.3.3.b California Regulations

Title 17 (Public Health, Division 3, Air Resources, Chapter 1, Air Resources Board, Subchapter 7.5, Airborne Toxic Control Measures; §93103, Regulation for Chromate Treated Cooling Towers) bans the use of hexavalent chromium containing compounds in cooling tower circulating water. For existing towers, especially wood towers, which have used such compounds in the past, a period of time is permitted to allow the chemicals to desorb from the tower and be eliminated so long as the level in the circulating water does not go above 0.15 mg/l (8 mg/l for wood towers) and tests show a continuous decrease over time.

3

TECHNICAL FEASIBILITY

3.1 Introduction

The technical feasibility and economics of using degraded water for cooling towers is evaluated in this section. Three hypothetical case studies of power plants using degraded water for cooling are discussed and evaluated in detail. The case studies include process wastewater, agricultural return water and reclaimed municipal effluent. Water consumption, water treatment equipment, chemicals requirements, cooling tower blowdown, solid-waste generation, operating costs and order-of-magnitude capital costs are identified for each case study. All case studies are evaluated against freshwater for comparative purposes and to benchmark the cost analysis.

Water, which would otherwise be usable for domestic or industrial purposes such as contaminated groundwater, is not evaluated in this section. After routine pre-treatment, e.g. air stripping, it was assumed that this type of water likely would not present any significant technological barriers for use as cooling tower make-up.

There are also types of contamination that are currently not fully understood with respect to health hazards, e.g. trace levels of manmade or natural complex organic compounds found in groundwater or surface water. Scenarios involving these possible forms of contamination are not evaluated in this report because there are no existing regulatory standards nor are there water quality criteria for use in cooling (or general industrial use). Therefore, treatment approaches for these types of contamination cannot be evaluated.

Other than a few examples of treated municipal effluent being used for cooling tower make-up (refer to Section 1, Introduction), degraded water is not typically used for power plant cooling in California. “Difficult” waters containing high levels of hardness, alkalinity, silica, salinity, etc. are commonly considered unusable when water source options are being evaluated for a power plant, especially when fresh water is available. Fresh water is typically selected for cooling, because special water treatment equipment is usually not required (e.g. softening, silica removal, etc.), specialty chemical treatment is usually straightforward, cooling system materials of construction are less costly (e.g. condenser metallurgy) and overall cooling system operation is more forgiving when water quality control problems are encountered.

Three case studies of power plants using degraded water for cooling are discussed and evaluated in detail in this section. The case studies include process wastewater from oil production, agricultural return water and reclaimed municipal effluent.

The degraded water scenarios are admittedly “difficult” from a freshwater treatment perspective, but as illustrated by the case studies, they are usable with appropriate treatment.

3.2 Case Studies

Three degraded water case studies are evaluated in this section of the report:

- Produced water - saline process wastewater generated by oil production
- Agricultural return water - saline water generated by flood irrigation
- Reclaimed water - treated municipal effluent generated in urban areas

In addition to evaluating degraded water case studies, fresh water is also evaluated. At the end of this section, degraded water and fresh water treatment requirements, chemical consumption, sludge generation and cost data are compared.

Refer to Table 3-1 for a summary of the chemical analysis. These specific analyses are also discussed in Table 2-5 and Section 2.3.3.c, Water Supply Screening. These waters (actual waste streams in California) were selected because they pose significant treatment problems, and with the exception of reclaimed water, are almost always considered unusable for cooling tower make-up. Each of the above source categories generates large volumes of wastewater, therefore, supply is not an issue. For the purpose of discussion, a different location was assigned for each scenario - Central Valley, desert and coastal plant settings. Central Valley and desert locations require extensive water treatment for cooling water to achieve high cycles of concentration to minimize blowdown generation. Cooling tower blowdown usually requires containment via evaporation ponds at inland plants. Also, desert plants benefit from more ambient evaporation (50 percent more) than plants in the Central Valley. Depending on the source water and power plant location (i.e. property available for evaporation ponds), post-treatment utilizing evaporators or crystallizers may be required to further reduce wastewater volume. Therefore, maximizing cooling system cycles of concentration for inland locations is assumed to be mandatory. The location assignments follow:

Case Study 1 - the Central Valley - Produced Water. This type of process wastewater is generated on a large-scale in certain area of the valley. (There are also areas where freshwater is “imported” for oil production). The water is characterized by high salinity and silica, moderate to high hardness and trace levels of ammonia and sulfide.

Case Study 2 - the Desert - Agricultural Return Water. This assignment is not as geographically correct as the other scenarios because agricultural activities are not widespread but clustered in the desert. Return water has high levels of dissolved salts, hardness, silica and moderate to high levels of phosphate, and as such, is analogous to degraded saline groundwater.

Case Study 3 - a Coastal Plant - Reclaimed Water. Most large metropolitan centers in California are located on the coast and reclaimed municipal effluent is a viable source of degraded water. Also, many municipal plants will consider post-treatment for ammonia removal to enable re-use. Reclaimed water has low to moderate salinity, hardness and silica. Phosphate and ammonia concentrations can be problematic.

Table 3-1
Source Water and Limiting Water Quality Criteria

	Units	Produced Water (Central Valley)	Ag Return Water (Desert)	Reclaimed Water (Coast)	Fresh Water
Na (by difference)	mg/l	982	2,182	76	41
K	mg/l	22	6	5	1
Ca	mg/l	40	554	76	18
Mg	mg/l	13	270	43	1
HCO ₃	mg/l	1,100	239	396	92
Cl	mg/l	920	1,480	102	22
SO ₄	mg/l	110	4,730	68	31
NO ₃	mg/l	NA ⁽⁶⁾	48	NA	NA
t-PO ₄ (8)	mg/l	NA	2	6	NA
S	mg/l	6	NA	NA	NA
SiO ₂	mg/l	120	37	17	16
B ⁽⁵⁾	mg/l	21	14	3	0.17
NH ₃	mg/l	5	NA	5	NA
TDS	mg/l	3,433	9,628	806	223
TSS	mg/l	<1	11	8	<1
BOD	mg/l	30	3	8	NA
COD	mg/l	80	32	5	NA

Screening-Level Cycles of Concentration - N - without Pre-Treatment

(Refer to Tables 2-3a and 2-3b for basic criteria and Table B-2 for evaluation formulas)

Cooling Tower Parameters

Cooling Tower Alkalinity, mg/l CaCO ₃	200	51	51	200
Calculated pH	7.9	7.0	7.0	7.9
Cooling Tower Hot-Side Temperature, °F	115	115	115	115
Langelier Saturation Index @ N = 5	1.2	0.9	0.1	1.0
Ryznar Stability Index @ N = 5	5.4	5.3	6.9	5.9

Cycles of Concentration

Ca (alone)	9.0	<1	4.7	20.0
Ca x SO ₄ (7)	3.6	<1	4.2	16.4
Mg x SiO ₂	3.4	1.3	5.0	38.7
SiO ₂	1.3	4.1	8.8	9.4
Ca (in presence of PO ₄ , assume pH = 7)	NA	<1	1.1	NA
TDS (35,000 mg/l maximum)	10.2	3.6	43.4	157.0

Notes.....

1. Produced water from oil production in the Central Valley.
2. Agricultural return water from the San Luis Drain.
3. Secondary-treated reclaimed water from the Bay Area. t-PO₄, B, NH₃ and COD were estimated.
4. West Kern water. Silica concentration was modified for this analysis.
5. B exists as H₃BO₃ (non-dissociated boric acid) in water at this pH.
6. NA = not applicable.
7. H₂SO₄ used for pH control is accounted for when calculating the impact of additional SO₄ on CaSO₄ solubility.
8. Total phosphate concentration.

3.3 Evaluation Basis

The parameters described in the evaluation basis were used for the three hypothetical case studies. Refer to Table 3-2 for a summary of evaluation parameters used throughout this section. Refer again to Table 3-1 for a summary of chemical analyses of the degraded water and fresh water sources evaluated. The table also includes a screening summary of critical water quality parameters (used to select treatment alternatives for each source water).

3.4 Case Study 1 - the Central Valley - Produced Water

Produced water is a byproduct of oil production. Low-quality steam is injected into a producing reservoir where it is utilized to loosen and fluidize oil from oil-bearing rock or sand. Oil and water return to the surface where they are separated. The water is de-oiled, filtered, softened and re-injected as steam. Many reservoirs produce excess water which must be disposed of (some fields generate significant volumes of wastewater). Excess produced water is disposed of in salt sinks via percolation where groundwater is markedly saline or it is injected into non-producing zones. Salt sinks could also be considered a source of degraded water. Refer to Table 3-1 for a chemical analysis of produced water. Depending on the reservoir, hardness, silica and salinity can be significantly higher than shown in the table. One example of variability is TDS which is a measure of total salt content. Depending on location, produced water TDS can range from 500 mg/l to 15,000 mg/l in the Central valley.

General Concerns

Based on the screening analysis located at the bottom of Table 3-1, if the produced water is untreated, it is limited by calcium sulfate solubility (CaSO_4) to 3.6 cycles of concentration in the cooling tower, magnesium/silica solubility product ($\text{Mg} \times \text{SiO}_2$) to 3.4 cycles, and silica solubility (SiO_2) to 1.3 cycles. Refer to Table B-2 in Appendix B for the formulas used to calculate maximum allowable cycles of concentration. Note, these formulas are considered conservative and detailed analysis (involving common ion effects, solubility temperature adjustments, ionic strength adjustments), as discussed in Section 2.3.3.b, Water Quality Prediction Software, would yield less restrictive criteria.

Calcium and magnesium concentrations are relatively low in this specific water, but the silica concentration is exceedingly high (high silica is typical for produced water). Although the sulfate in the source water is relatively low, a significant amount of sulfuric acid must be added to the cooling tower make-up to reduce the very high level of alkalinity (for calcium carbonate scale control in the cooling tower). This requirement significantly increases the sulfate concentration to the cooling tower. Also, ammonia poses a problem at 5 mg/l in the source water as it relates to wetted-surface metallurgy selection and biological control. Lastly, sulfide, BOD and COD are present and may effect the consumption of biological control chemicals.

Table 3-2
Evaluation Basis

1.	500 MW Gas-Fired Combined Cycle	
2.	Cooling System	
S	Cross-Flow Mechanical Draft Tower	
S	Cooling Water Recirculation Rate, gpm	128,000
S	Air Flow, SCFM	25,000,000
S	Evaporation Rate, gpm	1,750
S	Drift Rating, Pct of Recirculation Rate	0.002% (1)
S	Drift Rate, gpm	2.6
3.	Ambient Evaporation Data (for evaporation pond sizing)	
S	Central Valley, Class A Pan, inches/year	80
S	Central Valley, Adjusted Pan, inches/year	40 (2)
S	Desert, Class A Pan, inches/year	120
S	Desert, Adjusted Pan, inches/year	60 (2)
4.	Chemical Costs (3)	
S	90% Lime (CaO), \$/ton	\$155
S	98% Soda Ash (Na ₂ CO ₃), \$/ton	\$320
S	98% Sulfuric Acid (H ₂ SO ₄), \$/ton	\$180
S	100% Magnesium Chloride (MgCl ₂), \$/ton	\$260
S	Coag Aide (cationic polymer), \$/pound	\$3.00
S	Chlorine Dioxide (ClO ₂), \$/pound	\$1.00 (4)
S	Sodium Hypochlorite (NaOCl), \$/pound	\$0.35 (4)
S	Specialty Chemical Formulation, \$/pound	\$0.35 (4,6)
5.	Power, \$/kwh	\$0.08
6.	Sludge Disposal	
S	Transportation, \$/cubic yard	\$20
S	Disposal, \$/ton	\$50
7.	Operator Labor Costs, \$/hour (fully burdened)	\$35
8.	Water Costs	
S	Produced, Agricultural Return Water, \$/acrefoot	\$50
S	Reclaimed Water, \$/acrefoot	\$250
S	Fresh Water, \$/acrefoot	\$500
S	Demineralized Water Credit, \$/1000 gallons	\$2.10 (5)
9.	Amortization @ 7% for 30 years.	

Notes.....

1. Percent of cooling tower recirculation rate (manufacturer's rating).
2. Adjusted pan data accounts for losses in evaporation efficiency as a result of evaporation pond depth, increased salinity over time, etc.
3. Estimated delivered costs.
4. Dry basis.
5. Assumes treatment with RO and MB bottles - operating costs and capitalization (\$0.60/1,000 gal) plus cost of fresh water (\$1.50/1,000 gal).
6. Formulation blend of corrosion inhibitor, scale inhibitor and dispersant.

Treatment

Make-up softening was not considered because of the relatively low hardness of the source water. Side-stream softening was selected to benefit from the higher levels of hardness in the cooling water, i.e. magnesium precipitation is required for silica removal. Refer to Table 3-3 for a summary of operating chemistry (as well as water quality criteria, chemical feed requirements, flow rates, etc.). Side-stream softening is applied to a small portion of condenser return water to take advantage of the temperature of the water which should be at 105 to 115°F. Silica reduction is dramatically improved at higher temperatures. Refer to Figure 3-1 (middle figure, Side-Stream Softening) for a schematic representation of the process as it relates to the cooling system (this figure will be used for all case studies).

Also, refer to Section 5.3, Pre-, Side-Stream and Post-Treatment Technologies for a discussion of the side-stream reactor clarifier process and Appendix C for operating and performance parameters of this treatment technology (i.e. expected effluent chemistry and chemical requirements).

At a TDS limit of 35,000 mg/l (which is analogous to seawater salinity) for the cooling system, 10.3 cycles of concentration are achievable. This limit was set because there is a significant amount of metallurgical experience at this concentration, and at 10.3 cycles of concentration, the resulting blowdown rate is relatively low, 185 gpm. Recall, minimizing blowdown is critical to inland plants to reduce costly wastewater treatment and storage in evaporation ponds. The TDS limit could have been set at 70,000 mg/l for a blowdown rate of 93 gpm, but this would have forced metallurgical requirements to their practical limits, e.g. titanium heat exchanger metallurgy, non-metallic materials of construction for wetted surfaces wherever possible, etc.

The side-stream softener was sized at 3,008 gpm based on a parametric analysis conducted using the silica removal data presented in Figure 5-12, Final Silica vs Mg Precipitation. Using the data in Figure 5-12, it was determined that a magnesium precipitation level of 175 mg/l_{CaCO₃} yielded the most efficiently sized softener (design point is the “knee” of the capacity curve). Refer to Figure 3-2. Also, because there is an insignificant amount of magnesium in the feedwater, magnesium chloride (MgCl₂) must be added to supplement magnesium floc formation.

Table 3-3
Cooling Water Chemistry - Case Study 1

Produced Water		Cycles of Concentration = 10.28			
	Units	Make-up	Acidified Make-up	Cooling Water	Side-Stream Softener Effluent
Na by Diff	mg/l _{CaCO3}	2,131	2,131	25,711	25,948
K	mg/l _{CaCO3}	28	28	289	289
Ca	mg/l _{CaCO3}	100	100	93	35
Mg	mg/l _{CaCO3}	54	54	108	80
HCO ₃	mg/l _{CaCO3}	902	5	120	0
CO ₃	mg/l _{CaCO3}	0	0	0	120
OH	mg/l _{CaCO3}	0	0	0	4
Cl	mg/l _{CaCO3}	1,297	1,297	15,695	15,843
SO ₄	mg/l _{CaCO3}	114	1,011	10,386	10,386
NO ₃	mg/l _{CaCO3}	ND	ND	ND	ND
t-PO ₄	mg/l _{PO4}	ND	ND	ND	ND
S (5)	mg/l _S	6	6	12	12
SiO ₂	mg/l _{SiO2}	120	120	150	82
B	mg/l _B	21	21	216	216
NH ₃	mg/l _N	5	5	51	51
pH		7.0	5.8	7.5	10.0
TDS	mg/l	3,433	3,202	34,800	34,843
TSS	mg/l	<1	<1	10-20	<3
BOD	mg/l	30	30	(Note 4)	
COD	mg/l	80	80		

Pct of Limit.....

CaxSO ₄	75%
MgxSiO ₂	22%
SiO ₂	100%
K ₂ SPCa ₃ (PO ₄) ₂ Saturation	NA
LSI (Target Range = -1 to +1)	-0.07
RSI (Target Range = +6 to +7)	7.69

General Plant Data.....

Make-up, gpm	1,928
Blowdown, gpm	185
Side-Stream Softener Feed, gpm	3,008
45% Sludge, tons/day	19.0

Chemical Feed Requirement.....

Na ₂ CO ₃ , tons/day (1)	4.63	
CaO, tons/day (1)	1.77	
MgCl ₂ , tons/day (2)	2.54	
H ₂ SO ₄ , tons/day	10.37	
Coagulant Aide, pounds/day	108	
Specialty Chemical, pounds/day	575	(15 mg/l in cooling tower)

Notes.....

1. Refer to Appendix B, softener performance calculations - US Filter Technical Data Book, Section 57, Case 2.
2. Must add an equivalent amount of lime & soda ash for MgCl₂ usage.
3. ND = non detectable.
4. BOD and COD not quantifiable in the cooling tower.
5. Sulfide in cooling system is estimated - significant losses to air flow.

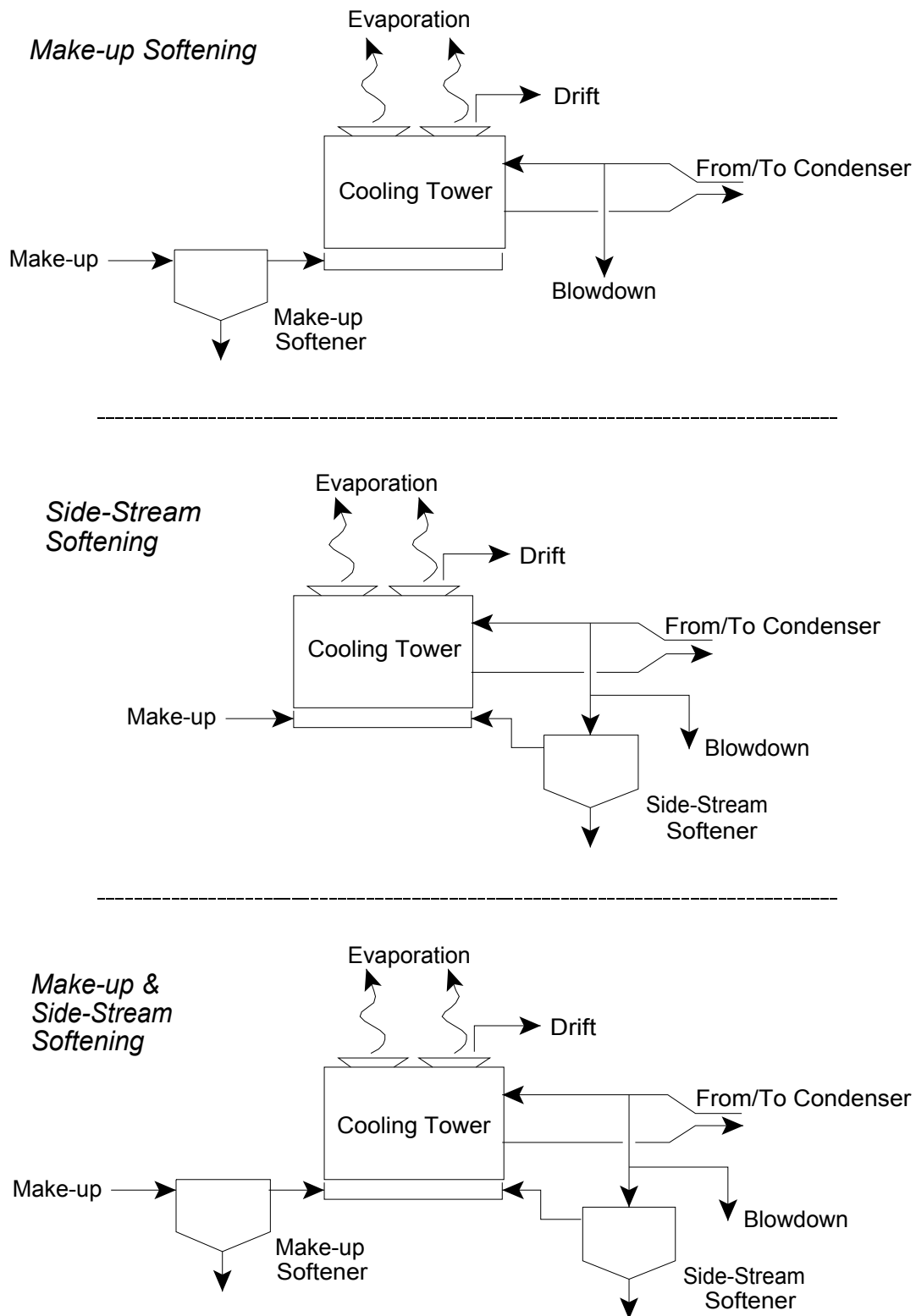


Figure 3-1
Make-Up Softening, Side-Stream Softening, Make-Up and Side-Stream Softening

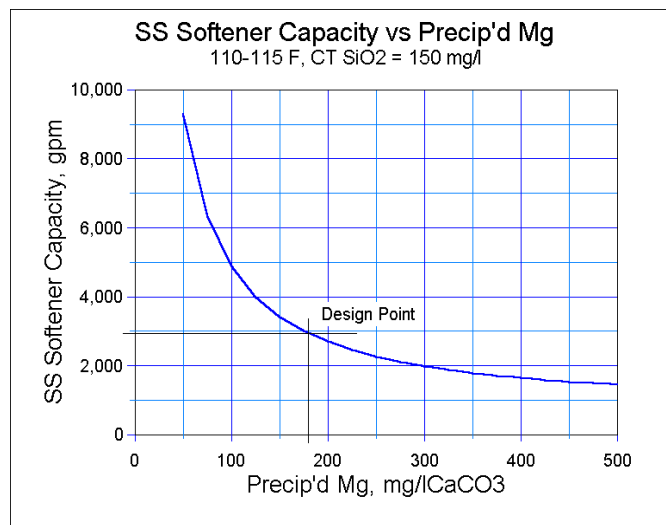


Figure 3-2
SS Softener Capacity vs Precip'd Mg

Cooling System Issues

Based on the cooling tower chemistry presented in Table 3-3, silica is the limiting water quality parameter for the cooling tower. Calcium sulfate solubility and the magnesium/silica solubility product are well below saturation levels. Because ammonia is present at fairly high levels, 90-10 copper-nickel is recommended for the cooling system metallurgy. Copper alloys (yellow metal) such as admiralty brass should be avoided. Chlorine dioxide (ClO₂) should be used for biological control because it does not react with ammonia. Bromination should not be considered for microbiological control because of the possibility of forming brominated organic compounds (bromine reacts with ammonia but the product is unstable and reverts to OBr⁻). It should be noted that biological control will be critical because of the favorable nutrient characteristics of ammonia. Cooling tower pH was purposely adjusted to 7.5 (120 mg/l_{CaCO₃} alkalinity) to allow sulfides to associate to their volatile form (25 percent as H₂S) in the circulating water. This should allow the air flow in the cooling tower to remove most of the sulfides and minimize oxidation by ClO₂ (sulfides readily react with oxidizing biocides). There will be a substantial dilution effect of the air stream which should render H₂S concentrations to non-detectable levels. Also a significant amount of sulfide will be lost in the vicinity of sulfuric acid addition where feedwater pH drops to 5.8. BOD and COD concentrations will be difficult to predict in the cooling tower, because some COD and BOD will be "consumed" by the cooling tower (oxidation via air flow and through biological activity). COD, however, may present a problem for chlorine dioxide consumption, but as stated previously, some of the COD will be consumed. Typically organic carbon in produced water is a mostly a mixture of aliphatic compounds (open chain). Since chlorine dioxide does not oxidize these compounds, this should not be a source of unnecessary ClO₂ consumption. A residual of a 1-mg/l equivalent of free available chlorine should be maintained twice per day for at least two hours per application. This should keep biological growth within control. Lastly, because of the potential for biological

growth, a wide-spaced film fill (low surface area to volume ratio) or traditional packing should be utilized in the cooling tower.

The specialty chemical program should focus on corrosion control because of high circulating water salinity and relatively low calcium hardness, alkalinity and pH. A biodispersant should be considered to prevent biological masses from adhering to cooling tower fill.

Operating Costs

Based on the chemical consumption rates presented in Table 3-3, side-stream softening should cost \$3,976 per day to operate. The reactor clarifier will generate 19.0 tons per day of sludge (45 percent solids by weight). Equipment amortization costs for the side-stream softener should amount to \$412 per day (equipment installation costs are discussed next). Cooling tower chemicals and produced water will cost \$3,293 per day. Estimates of chlorine dioxide demand should be tripled to account for COD demand and vigorous biological growth. To maintain a residual of 1.3 mg/l of chlorine dioxide (1-mg/l equivalent of $\text{OCl}^{\cdot-}$) in 128,000 gpm of recirculating water for a total of four hours per day requires 1,001 pounds per day (triple calculated demand). Refer to Table 3-4 for an operating cost summary for Case Study 1. The side-stream softener must receive at least 2 to 3 hours of attention per shift to ensure adequate operation. Likewise, cooling system chemistry should be checked twice per shift to ensure that water quality parameters are within specification. Cooling tower blowdown should be automated (controlled continuously) based on circulating water conductivity (salinity).

Specialty chemical usage was estimated on a formulation basis - a combination of corrosion inhibitor, scale inhibitor and dispersant (assumed for all cases including the base case). Since individualized treatment programs are site specific, it was felt that a generalized approach was more appropriate for this analysis. Also, specialty chemicals are consumed by the side-stream softening and lost to blowdown. The cost of specialty chemicals in this case study is significant, \$1,724 per day, because of the size of the side-stream softener.

Lastly, even though it is saline and considered wastewater, the cost assigned to produced water (as well as agricultural return water) assumes it has “intrinsic value” as a necessary commodity for power generation, and therefore, has commercial value.

Table 3-4
Case Study 1 - Produced Water - Treatment Cost Summary

90% Lime, \$/day	\$275	
98% Soda Ash, \$/day	\$1,482	
100% Magnesium Chloride, \$/day	\$659	
Coagulant Aide, \$/day	\$325	
Specialty Chemical Formulation, \$/day	\$1,724	
Sludge Disposal, \$/day	\$1,235	
Water Treating Chemicals, \$/day	\$5,700	
Softener Amortization Cost, \$/day	\$353	
Produced Water Cost, \$/day	\$426	
98% Sulfuric Acid, \$/day	\$1,866	
Chlorine Dioxide, \$/day	\$1,001	
Total Cooling Tower (basic chemicals)	\$3,293	
	\$9,346	(\$3.39/1000 gallons)
Total Treating Costs, \$/day	+8993\$	
	8,99\$8	
	,993	

Equipment Costs

Refer to Figure 5-13, Installed Cost vs Capacity, to estimate the cost of the 3,008 gpm side-stream softener (reactor clarifier). The softener should cost approximately \$1,600,000 installed (includes peripheral equipment - chemical silos and feeders and sludge handling and dewatering).

Three waste disposal alternatives were evaluated for this case study:

- Evaporation ponds only
- Evaporator with evaporation ponds
- Evaporator and crystallizer with no evaporation ponds

Assuming the plant is operated on a water conservation basis, many streams will be routed to the cooling tower, e.g. boiler blowdown, plant wash down ,etc. If we assume that an additional 5 percent of wastewater will be generated that cannot be routed to the cooling tower because of water quality concerns, then plant wastewater generation will be approximately 194 gpm.

Based on the adjusted pan data for evaporation of 40 inches per year for the Central Valley, 0.49 acres are required for every gallon per minute of wastewater disposed to the evaporation pond. Therefore, 95 acres of ponds are required to contain and evaporate the plant wastewater. Note,

flat terrain is required for evaporation ponds. At \$350,000 per acre (includes cost of land), evaporation ponds would cost \$33,300,000.

An evaporator will reduce the plant wastewater stream by 90 percent to 19.5 gpm. Also, 174.5 gpm of high-quality distillate would be produced (less 2 mg/l TDS) and could be used for boiler feedwater (a credit of \$2.10 per 1,000 gallons of distillate is applied in the following cost summary). The evaporator will cost approximately \$4,500,000 installed. Refer to Figure 5-13, Installed Cost vs Capacity, to estimate the cost of the evaporator. Power consumption would amount to 22,600 kwh per day (at 90 kwh per 1,000 gallons of product water) for a connected load of 940 kw. Power would cost \$1,808 per day (\$6.44 per 1,000 gallons of evaporator feedwater). A 9.6 acre evaporation pond would be required for evaporator concentrate at a cost of \$3,400,000.

A crystallizer would eliminate the need for an evaporation pond. A 19.5 gpm crystallizer would cost approximately \$1,100,000 installed. At 200 kwh per 1,000 gallons of product water, power consumption for the crystallizer would be 5,620 kwh per day (235 kw connected load) for a cost of \$450 per day (\$16.03 per 1,000 gallons of crystallizer feedwater).

Summarizing the results of evaluating waste disposal options (refer to Table 3-5), an evaporator and crystallizer combination will dramatically reduce waste treatment costs. Amortization costs were calculated based on a cost of money of 7 percent and a debt repayment period of 30 years.

Three-shift operation should be assigned to the plant for the water-related systems to monitor cooling tower chemistry, side-stream softener, evaporator and crystallizer. A dedicated crew of five operators would be required to oversee the systems full time (three shifts, 365 days per year) for a daily cost of \$997 per day.

Lastly, the installed costs in Table 3-5 below are considered order-of-magnitude estimates with an accuracy of +50/-35 percent, i.e. the costs could be 50 percent higher or 35 percent lower.

3.5 Case Study 2 - the Desert - Agricultural Return Water

Return water is wastewater generated by flood irrigation (which is practiced in many areas of California). Irrigation water is applied between deep furrows and is collected in tile drains several feet below the surface. Drainage canals carry the return water to disposal points, e.g. into rivers or man-made marshes. Refer to Table 3-1 for a chemical analysis of return water. Depending on the drainage system and location of irrigation, hardness, silica and salinity can vary significantly from that shown in the table.

Table 3-5
Case Study 1 - Produced Water - Disposal Cost Summary

	Evap Pond Only	Evaporator & Evaporation Pond	Evaporator & Crystallizer
Evaporation Pond, acres	95	9.6	NA
Evaporator Feed, gpm	NA	194	194
Crystallizer Feed, gpm	NA	NA	19.5
Installed Cost	\$33,300,000	\$7,900,000	\$5,600,000
Amortization Cost, \$/day	\$7,353	\$1,736	\$1,237
Power Requirement, kw	NA	940	1,175
Power Cost, \$/day	NA	\$1,808	\$2,258
Dedicated Labor Cost, \$/day	NA	\$997	\$997
Demineralized Water Credit, \$/day	NA	(\$528)	(\$587)
Operating Cost, \$/day	NA	\$2,277	\$2,668
Amortization + Operating, \$/day	\$7,353	\$5,205	\$4,612

General Concerns

Based on the screening analysis located at the bottom of Table 3-1, if the agricultural return water is untreated, it is limited by calcium sulfate solubility (CaSO_4) to less than 1 cycle of concentration in the cooling tower, magnesium/silica solubility product ($\text{Mg} \times \text{SiO}_2$) to 1.3 cycles, silica solubility (SiO_2) to 4.1 cycles and calcium phosphate solubility to less than 1 cycle. Refer to Table B-2 in Appendix B for the formulas used to calculate maximum allowable cycles of concentration.

Calcium, magnesium, sulfate and TDS concentrations are very high in this specific water. Because of the high TDS, the water is severely limited for cooling, i.e. even at a TDS control level of 35,000 mg/l, only 3.5 cycles of concentration are achievable with return water. Therefore, the analysis is based upon fresh water being blended in equal portions (50-50) with return water to dilute return water to allow higher cycles of concentration. Refer again to Table 3-1 for the chemical analysis of fresh water.

Treatment

Make-up softening is utilized because of the high hardness of the source water. Even when blended with low hardness fresh water, the return water hardness exceeds 1,270 mg/l_{CaCO₃}. Refer to Table 3-6 for a summary of operating chemistry (as well as water quality criteria, chemical feed requirements, flow rates, etc.). Side-stream softening was also selected to further reduce hardness to satisfy calcium sulfate solubility limitations (as discussed previously, these limits are conservative). Note, calcium sulfate solubility is at 240 percent of maximum (this excess can be controlled with crystal modifiers and scale dispersants). If an excess of 600 to 700 percent of calcium sulfate could be tolerated (with crystal modifiers and scale dispersants), the side-stream soften could be eliminated. Refer to Figure 3-1 (bottom figure, Make-up & Side-Stream Softening) for a schematic representation of the process as it relates to the cooling system.

Also, refer to Section 5.3, Pre-, Side-Stream and Post-Treatment Technologies for a discussion of the make-up and side-stream reactor clarifier processes and Appendix C for operating parameters and performance of this technology (i.e. expected effluent chemistry and chemical requirements).

An operating TDS of 50,000 mg/l was selected for the cooling system. This will allow 10.3 cycles of concentration. This limit was set because blowdown has a significant impact on disposal and post-treatment costs as presented in Case Study 1 (if the TDS limit were set at 35,000 mg/l, blowdown would increase by 30 percent). At 50,000 mg/l salinity, titanium heat exchanger metallurgy and non-metallic materials of construction will be required wherever possible.

Cooling System Issues

Based on the cooling tower chemistry presented in Table 3-6, calcium sulfate is the limiting water quality parameter for the cooling tower. Calcium phosphate would have been a concern but make-up softening removes phosphate to non-detectable or very low levels. Any phosphate that may be generated by the degradation of organo-phosphates, which could be used for scale inhibition, should be removed by the side-stream softener. The magnesium/silica solubility product and silica are well below saturation levels. Sodium hypochlorite (NaOCl) should be utilized for biological control. Unlike produced water in Case 1, there are no concerns with ammonia (recall, every mg/l of ammonia consumes 10 mg/l of NaOCl). BOD and COD concentrations will be difficult to predict in the cooling tower, because some COD and BOD will be “consumed” by the cooling tower (oxidation via air flow and through biological activity). COD, however, may present a problem for chlorine consumption, but as stated previously, some of the COD will be consumed. A residual of a 1-mg/l equivalent of free available chlorine should be maintained twice per day for at least two hours per application. This should keep biological growth within control. Lastly, because of the potential for biological growth (BOD could provide some nutrient stimulation), a wide-spaced film fill (low surface area to volume ratio) or traditional packing should be used utilized in the cooling tower.

Table 3-6
Cooling Water Chemistry - Case Study 2

Agricultural Return Water/Fresh Water Blend				Cycles of Concentration = 10.28				
	Units	50% Ag Return Make-up	50% Fresh Make-up	Blended Make-up	Softened Blended Make-up	Acidified Make-up	Cooling Water	Side-Stream Softener Effluent
Na by Diff	mg/l _{CaCO3}	4,735	89	2,412	3,484	3,484	36,213	36,414
K	mg/l _{CaCO3}	8	1	4	4	4	44	44
Ca	mg/l _{CaCO3}	1,385	45	715	35	35	123	35
Mg	mg/l _{CaCO3}	1,112	3	558	80	80	281	80
HCO ₃	mg/l _{CaCO3}	196	75	136	0	49	136	0
CO ₃	mg/l _{CaCO3}	0	0	0	45	0	0	45
OH	mg/l _{CaCO3}	0	0	0	4	0	0	4
Cl	mg/l _{CaCO3}	2,087	31	1,059	1,059	1,059	10,882	10,882
SO ₄	mg/l _{CaCO3}	4,919	32	2,476	2,476	2,476	25,443	25,443
NO ₃	mg/l _{CaCO3}	39	NA	19	19	19	199	199
t-PO ₄	mg/l _{PO4}	2	NA	1	ND	ND	ND	ND
S	mg/l _S	NA	NA	NA	NA	NA	NA	NA
SiO ₂	mg/l _{SiO2}	37	16	27	13	13	39	3
B	mg/l _B	14	0.17	7	7	7	73	73
NH ₃	mg/l _N	NA	NA	NA	NA	NA	NA	NA
pH		7.5	7.2	7.3	10.0	7.2	7.6	10.0
TDS	mg/l	9,628	222	4,925	4,880	4,911	49,891	49,726
TSS	mg/l	11	<1	6	<3	<3	10-20	<3
BOD	mg/l	3	NA	1.5	1.5	1.5	(Note 4)	
COD	mg/l	32	NA	16	16	16		

Pct of Limit.....

CaxSO ₄	240%
MgxSiO ₂	15%
SiO ₂	26%
K _{SP} Ca ₃ (PO ₄) ₂ Saturation	NA
LSI - Target Range = -1 to +1	0.18
RSI - Target Range = +6 to +7	7.27

General Plant Data.....

Make-up, gpm	1,928
Blowdown, gpm	185
Side-Stream Softener Feed, gpm	506

	<u>Make-up</u>	<u>Side-Stream</u>	<u>Total</u>
45% Sludge, tons/day	49.7	5.3	55.0

Chemical Feed Requirement.....

Na ₂ CO ₃ , tons/day (1)	13.41	0.66	14.07
Ca(OH) ₂ , tons/day (1)	4.44	0.66	5.11
MgCl ₂ , tons/day (2)	0.00	0.00	0.00
H ₂ SO ₄ , tons/day	0.00	NA	0.00
Coagulant Aide, pounds/day	69	18	88
Specialty Chemical, pounds/day	124	(15 mg/l in cooling tower)	

Notes.....

1. Refer to Appendix B, softener performance calculations - US Filter Technical Data Book, Section 57, Class 1(Case 2) and Class 2.
2. Must add an equivalent amount of lime & soda ash for MgCl₂ usage.
3. ND = non detectable.
4. BOD and COD not quantifiable in the cooling tower.

The specialty chemical program should focus on corrosion control because of very high circulating water salinity and relatively low calcium hardness, alkalinity and pH. Also, a crystal modifier/dispersant should be used to control calcium sulfate scale formation. A biodispersant should be considered to prevent biological masses from adhering to cooling tower fill.

Operating Costs

Based on the chemical consumption rates presented in Table 3-6, make-up softening should cost \$8,417 per day to operate. Side-stream softening should cost \$712 per day to operate. The reactor clarifiers will generate 55.0 tons per day of sludge (45 percent solids by weight). Equipment amortization costs for the side-stream softener should amount to \$335 per day for the make-up softener and \$155 for the side-stream softener (equipment installation costs discussed next). Note, because the make-up and side-stream softeners removes essentially all of the alkalinity entering the cooling tower, sulfuric acid is not required to adjust cooling tower alkalinity (nonetheless, a sulfuric acid addition system should be installed). Cooling tower chemicals, freshwater and return water should cost \$2,734 per day. Estimates of chlorine dioxide demand should be tripled to account for COD demand and vigorous biological growth. To maintain a residual of 1 mg/l of free available chlorine (OCl^-) in 128,000 gpm of recirculating water for a total of four hours per day requires 1,117 pounds (dry basis) per day of sodium hypochlorite (triple calculated demand) Refer to Table 3-7 for an operating cost summary for Case Study 2. The side-stream softener must receive at least 2 to 3 hours of attention per shift to ensure adequate operation. Likewise, the cooling system chemistry should be checked twice per shift to ensure that water quality parameters are within specification. Cooling tower blowdown should be automated (controlled continuously) based on circulating water conductivity (salinity).

Equipment Costs

Refer to Figure 5-13, Installed Cost vs Capacity, to estimate the costs of the 1,928 gpm make-up softener and 506 gpm side-stream softener (reactor clarifier). The make-up softener should cost approximately \$1,300,000 installed and the side-stream about \$600,000 (includes peripheral equipment - chemical silos and feeders and sludge handling and dewatering).

Three waste disposal alternatives were evaluated for this case study:

- Evaporation ponds only
- Evaporator with evaporation ponds
- Evaporator and crystallizer with no evaporation ponds

Assuming the plant is operated on a water conservation basis, many streams will be routed to the cooling tower, e.g. boiler blowdown, plant wash down ,etc. If we assume that an additional 5 percent of wastewater will be generated that cannot be routed to the cooling tower because of water quality concerns, then plant wastewater generation will be approximately 194 gpm.

Based on the adjusted pan data for evaporation of 60 inches per year for the desert (0.33 acres per gpm of wastewater). Therefore, 64 acres of ponds are required to contain and evaporate the plant wastewater. At \$350,000 per acre, evaporation ponds would cost \$22,400,000.

Table 3-7
Case Study 2 - Agriculture Return Water - Treatment Cost Summary

	<u>Make-up</u>	<u>Side-Stream</u>
90% Lime, \$/day	\$688	\$102
98% Soda Ash, \$/day	\$4,291	\$211
100% Magnesium Chloride, \$/day	\$0	\$0
Coagulant Aide, \$/day	\$207	\$54
Specialty Chemical Formulation, \$/day	\$373	(Incl)
Sludge Disposal, \$/day	\$3,231	\$345
Water Treating Chemicals, \$/day	\$8,790	\$712
Softener Amortization Costs, \$/day	\$287	\$132
Agricultural Return Water	\$213	
Fresh Water, \$/day	\$2,130	
98% Sulfuric Acid, \$/day	\$0	
Sodium Hypochlorite, \$/day	\$391	
Total Cooling Tower (basic chemicals)	\$2,734	
Total Treating Costs, \$/day	\$12,655	(\$4.56/1000 gallons)

An evaporator will reduce the plant wastewater stream by 90 percent to 19.5 gpm. Also, 174.5 gpm of high-quality distillate would be produced (less 2 mg/l TDS) and could be used for boiler feedwater (a credit of \$2.10 per 1,000 gallons of distillate is applied in the following cost summary). The evaporator will cost approximately \$4,500,000 installed. Refer to Figure 5-13, Installed Cost vs Capacity, to estimate the cost of the evaporator. Power consumption would amount to 22,600 kwh per day (at 90 kwh per 1,000 gallons of product water) for a connected load of 940 kw. Power would cost \$1,808 per day (\$6.44 per 1,000 gallons of evaporator feedwater). A 6.4 acre evaporation pond would be required for evaporator concentrate at a cost of \$2,300,000.

A crystallizer would eliminate the need for an evaporation pond. A 19.5 gpm crystallizer would cost approximately \$1,100,000 installed. At 200 kwh per 1,000 gallons of product water, power consumption for the crystallizer would be 5,620 kwh per day (235 kw connected load) for a cost of \$450 per day (\$16.03 per 1,000 gallons of crystallizer feedwater).

Summarizing the results of evaluating waste disposal options (refer to Table 3-8), an evaporator with evaporation ponds provide the lowest waste treatment costs. Note, there is a small amortized cost increase with a crystallizer. Further detailed analysis would be required to

optimize waste treatment selection (especially given the order-of-magnitude accuracy of the analysis). Three-shift operation should be assigned to the plant for the water-related systems to monitor cooling tower chemistry, side-stream softener and evaporator. A dedicated crew of five operators would be required to oversee the systems full time (three shifts, 365 days per year) for a daily cost of \$997 per day.

Table 3-8
Case Study 2 - Agricultural Return Water - Disposal Cost Summary

	Evap Pond Only	Evaporator & Evaporation Pond	Evaporator & Crystallizer
Evaporation Pond, acres	64	6.4	NA
Evaporator Feed, gpm	NA	195	195
Crystallizer Feed, gpm	NA	NA	19.5
Installed Cost	\$22,400,000	\$6,700,000	\$5,600,000
Amortization Cost, \$/day	\$4,946	\$1,480	\$1,237
Power Requirement, kw	NA	940	1,175
Power Cost, \$/day	NA	\$1,804	\$2,256
Dedicated Labor Cost, \$/day	NA	\$997	\$997
Demineralized Water Credit, \$/day	NA	(\$528)	(\$587)
Operating Cost, \$/day	NA	\$2,273	\$2,666
Amortization + Operating, \$/day	\$4,946	\$3,753	\$3,903

3.6 Case Study 3 - a Coastal Plant - Reclaimed Water

Reclaimed water in the context of this report is filtered, treated municipal effluent. The water must be treated to meet California Title 22 standards for reuse as cooling tower make-up which requires tertiary treatment - secondary treatment (clarification, BOD and COD removal) followed by filtration and disinfection. Refer to Table 3-1 for a chemical analysis of reclaimed water. There are a significant number of wastewater treatment plants in California which are specifically designed for water reclamation and reuse of municipal effluent. Most of the treated effluent used for this purpose is generated in metropolitan areas and most of the reuse is applied to irrigation. However as discussed in Section 1, Introduction, there is some reclaimed water used for cooling tower make-up (most of it is for refinery cooling in southern California). Four planned power projects will utilize reclaimed water for cooling. Water quality parameters of treated effluent can vary significantly based on the fresh water supply in the area and contributors to the wastewater stream, i.e. the mix of household, commercial and industrial waste.

General Concerns

Based on the screening analysis located at the bottom of Table 3-1, if the agricultural return water is untreated, it is limited by calcium sulfate solubility (CaSO_4) to 4.2 cycles of concentration in the cooling tower, magnesium/silica solubility product ($\text{Mg} \times \text{SiO}_2$) to 5.0 cycles and calcium phosphate solubility to 1.1 cycles. Refer to Table B-2 in Appendix B for the formulas used to calculate maximum allowable cycles of concentration.

Since the setting for this plant is the California coast, high cycles of concentration in the cooling tower (resulting in less blowdown) are not an issue of concern. Therefore, a target of six cycles of concentration was set for the cooling tower. Note that power plants are required to obtain an NPDES permit if they discharge to state waters and must meet some very restrictive discharge requirements depending on the discharge location, e.g. Santa Monica Bay or San Francisco Bay. Many plants make an effort to route their wastewater (blowdown is usually the largest component of the waste stream) to a municipal treatment plant.

For the purpose of this analysis, it was assumed that phosphate and ammonia are not removed before the water is delivered to the power plant. Municipal treatment plants are capable of removing these constituents, but it requires additional treatment processes and/or process modifications which the majority of treatment plants do not employ. General mineral parameters such as hardness, sulfate, silica, etc. are not effected by the treatment processes utilized by municipal effluent plants.

Treatment

Make-up softening is utilized to remove phosphate from the feedwater to the cooling tower. Without softening phosphate levels are 40 times saturation at a pH of 7.0. Even with specialty chemicals, this type of barrier cannot be overcome. Softening removes phosphate from cooling tower make-up, thus eliminating it as an issue of concern. Other parameters, such as calcium, magnesium, sulfate and silica, are moderately low and do not pose scaling problems at six cycles of concentration. Refer to Table 3-9 for a summary of operating chemistry (as well as water quality criteria, chemical feed requirements, flow rates, etc.). Refer to Figure 3-1 (top figure, Make-up Softening) for a schematic representation of the process as it relates to the cooling system.

Also, refer to Section 5.3, Pre-, Side-Stream and Post-Treatment Technologies for a discussion of the make-up reactor clarifier process and Appendix C for operating parameters and expected performance of this technology (i.e. effluent chemistry and chemical requirements).

Table 3-9
Cooling Water Chemistry - Case Study 3

Reclaimed Water			Cycles of Concentration = 6.01		
	Units	Make-up	Softened Make-up	Acidified Make-up	Cooling Water
Na by Diff	mg/l _{CaCO3}	165	165	165	991
K	mg/l _{CaCO3}	6	6	6	38
Ca	mg/l _{CaCO3}	190	35	35	210
Mg	mg/l _{CaCO3}	177	87	87	523
HCO ₃	mg/l _{CaCO3}	325	0	33	200
CO ₃	mg/l _{CaCO3}	0	79	0	0
OH	mg/l _{CaCO3}	0	0	0	0
Cl	mg/l _{CaCO3}	144	144	144	864
SO ₄	mg/l _{CaCO3}	71	71	116	700
NO ₃	mg/l _{CaCO3}	ND	ND	ND	ND
t-PO ₄	mg/l _{PO4}	6	ND	ND	ND
S	mg/l _S	ND	ND	ND	ND
SiO ₂	mg/l _{SiO2}	17	12	12	72
B	mg/l _B	3	3	3	18
NH ₃	mg/l _N	5	5	5	30
pH		7.5	9.4	5.8	7.9
TDS	mg/l	806	363	400	2,402
TSS	mg/l	8	<3	<3	10-20
BOD	mg/l	8	8	8	(Note 4)
COD	mg/l	5	5	5	

Pct of Limit.....

CaxSO ₄	11%
MgxSiO ₂	50%
SiO ₂	48%
K _{SP} Ca ₃ (PO ₄) ₂ Saturation	NA
LSI - Target Range = -1 to +1	0.86
RSI - Target Range = +6 to +7	6.15

General Plant Data.....

Make-up, gpm	2,088
Blowdown, gpm	345
45% Sludge, tons/day	16.3

Chemical Feed Requirement.....

Na ₂ CO ₃ , tons/day (1)	0.00	
Ca(OH) ₂ , tons/day (1)	2.90	
MgCl ₂ , tons/day (2)	0.00	
H ₂ SO ₄ , tons/day	0.57	
Coagulant Aide, pounds/day	75	
Specialty Chemical, pounds/day	62	(15 mg/l in cooling tower)

Notes.....

1. Refer to Appendix B, softener performance calculations - US Filter Technical Data Book, Section 56.
2. Must add an equivalent amount of lime & soda ash for MgCl₂ usage.
3. ND = non detectable.
4. BOD and COD not quantifiable in the cooling tower.

Cooling System Issues

Based on the cooling tower chemistry presented in Table 3-9, ammonia is the only water quality parameter of concern in the cooling system. Calcium sulfate and magnesium/silica are well below saturation levels. At six cycles of concentration, the operating TDS of the cooling tower will be 2,400 mg/l. However, because of the presence of ammonia, 90-10 copper nickel should be employed for heat transfer surfaces. Carbon steel can be used for all other components in the cooling system. Copper alloys such as admiralty and brass should be avoided. Chlorine dioxide (ClO_2) should be utilized for biological control because it does not react with ammonia (bromination could also be used in the presence of ammonia). Biological control will be critical because of the favorable nutrient characteristics of ammonia. BOD and COD concentrations will be difficult to predict in the cooling tower, because some COD and BOD will be “consumed” by the cooling tower (oxidation via air flow and through biological activity). COD, however, may present a problem for chlorine dioxide consumption, and as stated previously, some of the COD will be consumed. A residual of a 1-mg/l equivalent of free available chlorine should be maintained twice per day for at least two hours per application. This should keep biological growth within control. If blowdown is discharged to state waters, de-chlorination must be employed to remove residual ClO_2 . Lastly, because of the potential for biological growth, a wide-spaced film fill (low surface area to volume ratio) or traditional packing should be used utilized in the cooling tower.

The specialty chemical program should focus on corrosion control to protect carbon steel components. A biocides program should be considered to prevent biological masses from adhering to cooling tower fill.

Operating Costs

Based on the chemical consumption rates presented in Table 3-5a, make-up softening should cost \$1,735 per day to operate. The reactor clarifiers will generate 16.3 tons per day of sludge (45 percent solids by weight). Equipment amortization costs for the make-up softener should amount to \$335 per day (equipment installation costs discussed next). Cooling tower chemicals and reclaimed water should cost \$3,411 per day. Because the make-up softener removes a significant amount of the alkalinity entering the cooling tower, sulfuric acid consumption is minimal. Estimates of chlorine dioxide demand should be tripled to account for COD demand and vigorous biological growth. To maintain a residual of 1 mg/l of free available chlorine

(OCl^{-1}) in 128,000 gpm of recirculating water for a total of four hours per day requires 1,001 pounds (dry basis) per day of sodium hypochlorite (triple calculated demand). Refer to Table 3-5b for an operating cost summary for Case Study 3. The make-up softener must receive at least 2 to 3 hours of attention per shift to ensure adequate operation.

Table 3-10
Case Study 3 - Reclaimed Water - Treatment Cost Summary

90% Lime, \$/day	\$450	
98% Soda Ash, \$/day	\$0	
100% Magnesium Chloride, \$/day	\$0	
Coagulant Aide, \$/day	\$225	
Specialty Chemical Formulation, \$/day	\$186	
Sludge Disposal, \$/day	\$1,060	
Water Treating Chemicals, \$/day	\$1,921	
Softener Amortization Costs, \$/day	\$287	
Reclaimed Water, \$/day	\$2,307	
98% Sulfuric Acid, \$/day	\$103	
Chlorine Dioxide, \$/day	\$1,001	
Total Cooling Tower (basic chemicals)	\$3,411	
Total Treating Chemicals, \$/day	\$5,619	(\$1.85/1000 gallons)

Likewise, the cooling system chemistry should be checked twice per shift to ensure that water quality parameters are within specification. Cooling tower blowdown should be automated (controlled continuously) based on circulating water conductivity (salinity).

Equipment Costs

Refer to Figure 5-13, Installed Cost vs Capacity, to estimate the costs of the 2,088 gpm make-up softener. The make-up softener should cost approximately \$1,300,000 (includes peripheral equipment - chemical silos and feeders and sludge handling and dewatering). Disposal costs were not evaluated since blowdown and other plant wastes will be discharged either to an outfall or to a municipal wastewater treatment plant. Installed costs for softening are considered order-of-magnitude estimates with an accuracy of +50/-35 percent, i.e. the costs could be 50 percent higher or 35 percent lower.

3.7 Base Case - Fresh Water

Fresh water was evaluated to compare operating and capital costs to the degraded water scenarios discussed previously. Refer to the fresh water analysis in Table 3-1. The chemical analysis for the fresh water source is commonly used in the southern part of Central Valley. The water is of relatively good quality - low hardness, low silica and low TDS. Two cases are evaluated for fresh water - inland plant and coastal plant. The inland plant will include two disposal scenarios - Central Valley setting (40 inches of adjusted pan evaporation) and a desert setting (60 inches of adjusted pan evaporation).

3.7.1 Base Case - Fresh Water - Inland Plant

Based on the screening analysis located at the bottom of Table 3-1, if fresh water is untreated, it is limited by silica (SiO_2) solubility to 9.4 cycles of concentration in the cooling tower. Refer to Table B-2 in Appendix B for the formulas used to calculate maximum allowable cycles of concentration.

The goal of this analysis, as with the other inland plants, was to reduce blowdown to a minimum achievable level. Side-stream softening is utilized to accomplish this. Make-up softening was not considered since the source water has very low hardness. The side-stream softener is utilized primarily to remove calcium and silica (magnesium chloride is also added to enhance silica removal). Refer to Figure 3-1 (middle figure, Side-Stream Softening) for a schematic representation of the process as it relates to the cooling system.

Treatment

The cycles of concentration for the cooling tower was set at 29.7 (58 gpm of blowdown). At this level with side-stream softening, only silica is at its maximum saturation level. Other parameters, such as calcium, magnesium and sulfate are moderately low and do not pose scaling problems. Refer to Table 3-11 for a summary of operating chemistry (as well as water quality criteria, chemical feed requirements, flow rates, etc.).

Note, 30 cycles of concentration is a practical limit for cooling towers. Above this level, slight variations in the blowdown rate can significantly vary cooling tower chemistry.

Also, refer to Section 5.3, Pre-, Side-Stream and Post-Treatment Technologies for a discussion of the side-stream reactor clarifier process and Appendix C for operating parameters and expected performance of this technology (i.e. effluent chemistry and chemical requirements).

Cooling System Issues

Based on the cooling tower chemistry presented in Table 3-11, silica is the only water quality parameter of concern in the cooling system. Calcium sulfate and magnesium/silica are well below saturation levels. At 29.4 cycles of concentration, the operating TDS of the cooling tower will be 6,800 mg/l. Admiralty brass type alloys can be employed for heat transfer surfaces. Carbon steel can also be used for all other components in the cooling system. Sodium hypochlorite (NaOCl) can be utilized for biological control. A residual of 1 mg/l of free available chlorine should be maintained twice per day for at least two hours per application. This should keep biological growth within control. The specialty chemical program should focus on corrosion control for carbon steel and copper alloy components.

Table 3-11
Cooling Water Chemistry - Fresh Water Case

Inland Plant			Cycles of Concentration = 29.73		
	Units	Make-up	Acidified Make-up	Cooling Water	Side-Stream Softener Effluent
Na by Diff	mg/l _{CaCO3}	89	89	4,591	4,843
K	mg/l _{CaCO3}	1	1	27	27
Ca	mg/l _{CaCO3}	45	45	260	35
Mg	mg/l _{CaCO3}	3	3	82	80
HCO ₃	mg/l _{CaCO3}	75	7	200	0
CO ₃	mg/l _{CaCO3}	0	0	0	45
OH	mg/l _{CaCO3}	0	0	0	4
Cl	mg/l _{CaCO3}	31	31	1,760	1,935
SO ₄	mg/l _{CaCO3}	32	101	3,001	3,001
NO ₃	mg/l _{CaCO3}	ND	ND	ND	ND
t-PO ₄	mg/l _{PO4}	ND	ND	ND	ND
S	mg/l _S	ND	ND	ND	ND
SiO ₂	mg/l _{SiO2}	16	16	150	82
B	mg/l _B	ND	ND	0	0
NH ₃	mg/l _N	ND	ND	0	0
pH		7	6.2	7.9	10.0
TDS	mg/l	221	204	6,789	6,655
TSS	mg/l	<3	<3	10-20	<3
BOD	mg/l	ND	ND	(Note 4)	
COD	mg/l	ND	ND		

Pct of Limit.....

CaxSO ₄	60%
MgxSiO ₂	16%
SiO ₂	100%
K _{SP} Ca ₃ (PO ₄) ₂ Saturation	NA
LSI - Target Range = -1 to +1	0.92
RSI - Target Range = +6 to +7	6.02

General Plant Data.....

Make-up, gpm	1,801
Blowdown, gpm	58
Side-Stream Softener Feed, gpm	290
45% Sludge, tons/day	1.7

Chemical Feed Requirement.....

Na ₂ CO ₃ , tons/day (1)	0.47	
Ca(OH) ₂ , tons/day (1)	0.41	
MgCl ₂ , tons/day (2)	0.29	
H ₂ SO ₄ , tons/day	0.74	
Coagulant Aide, pounds/day	10	
Specialty Chemical, pounds/day	63	(15 mg/l in cooling tower)

Notes.....

1. Refer to Appendix B: Softener performance calculations - US Filter Technical Data Book, Section 56.
2. Must add an equivalent amount of lime & soda ash for MgCl₂ usage.
3. ND = non detectable.
4. BOD and COD not quantifiable in the cooling tower.

Operating Costs

Based on the chemical consumption rates presented in Table 3-11, side-stream softening should cost \$432 per day to operate. Also, refer to Table 3-12 for an operating cost summary.

Table 3-12
Base Case - Fresh Water - Inland Plant - Treatment Cost Summary

90% Lime, \$/day	\$64
98% Soda Ash, \$/day	\$151
100% Magnesium Chloride, \$/day	\$75
Coagulant Aide, \$/day	\$31
Specialty Chemical Formulation, \$/day	\$188
Sludge Disposal, \$/day	\$111
Water Treating Chemicals, \$/day	\$620
Softener Amortization Costs, \$/day	\$88
Fresh Water, \$/day	\$3,980
98% Sulfuric Acid, \$/day	\$134
Sodium Hypochlorite, \$/day	\$196
Total Cooling Tower (basic chemicals)	\$4,310
Total Treating Costs, \$/day	\$5,018 (\$193/1000 gallons)

The reactor clarifier will generate 1.7 tons per day of sludge (45 percent solids by weight). Equipment amortization costs for the side-stream softener should amount to \$103 per day (equipment installation costs discussed next). Cooling tower chemicals and freshwater should cost \$4,310 per day. To maintain a residual of 1 mg/l of free available chlorine (OCl^{-1}) in 128,000 gpm of recirculating water for a total of four hours per day requires 559 pounds (dry basis) per day of sodium hypochlorite (1.5 times the calculated demand). The side-stream softener must receive at least 2 to 3 hours of attention per shift to ensure adequate operation. Likewise, the cooling system chemistry should be checked twice per shift to ensure that water quality parameters are within specification. Cooling tower blowdown should be automated (controlled continuously) based on circulating water conductivity (salinity).

Equipment Costs

Refer to Figure 5-13, Installed Cost vs Capacity, to estimate the costs of the 290 gpm side-stream softener. The softener should cost approximately \$400,000 (includes peripheral equipment - chemical silos and feeders and sludge handling and dewatering). Disposal cost scenarios for Central Valley and desert plants follow.

3.7.1.a Central Valley Plant - Disposal Costs

Assuming the plant is operated on a water conservation basis, many streams will be routed to the cooling tower, e.g. boiler blowdown, plant wash down ,etc. If we assume that an additional 5 percent of wastewater will be generated that cannot be routed to the cooling tower because of water quality concerns, then plant wastewater generation will be approximately 61 gpm.

Based on the adjusted pan data for evaporation of 40 inches per year for the Central Valley (0.49 acres are required for every qpm of wastewater). Therefore, 30 acres of ponds are required to contain and evaporate the plant wastewater. At \$350,000 per acre, evaporation ponds would cost \$15,500,000.

An evaporator will reduce the plant wastewater stream by 90 percent to 6.1 gpm. Also, 54.9 gpm of high-quality distillate would be produced (less 2 mg/l TDS) and could be used for boiler feedwater (a credit of \$2.10 per 1,000 gallons of distillate is applied in the cost summary). The evaporator will cost approximately \$2,300,000 installed. Refer to Figure 5-13, Installed Cost vs Capacity, to estimate the cost of the evaporator. Power consumption would amount to 7,120 kwh per day (at 90 kwh per 1,000 gallons of product water) for a connected load of 300 kw. Power would cost \$576 per day (\$6.56 per 1,000 gallons of evaporator feedwater). A 3 acre evaporation pond would be required for evaporator concentrate at a cost of \$1,050,000.

A crystallizer would eliminate the need for an evaporation pond. A 6.1 gpm crystallizer would cost approximately \$600,000 installed. At 200 kwh per 1,000 gallons of product water, power consumption for the crystallizer would be 1,757 kwh per day (75 kw connected load) for a cost of \$140 per day (\$15.94 per 1,000 gallons of crystallizer feedwater).

Summarizing the results of evaluating waste disposal options (refer to Table 3-13), it is clear that an evaporator/evaporation pond or an evaporator/crystallizer will reduce disposal costs. Note, there is practically no cost difference between the evaporator disposal options, so the simpler of the two alternatives was selected. Three-shift operation should be assigned to monitor cooling system chemistry, the side-stream softener, evaporator and crystallizer (if installed as a result of further analysis). A dedicated crew of five operators would be required to oversee the water systems for a daily cost of \$997 per day.

Table 3-13
Base Case - Fresh Water - Central Valley Inland Plant - Disposal Cost Summary

	Evap Pond Only	Evaporator & Evaporation Pond	Evaporator & Crystallizer
Evaporation Pond, acres	30	3	NA
Evaporator Feed, gpm	NA	61	61
Crystallizer Feed, gpm	NA	NA	6.15
Installed Cost	\$10,500,00	\$3,400,000	\$2,900,000
Amortization Cost, \$/day	\$2,319	\$751	\$640
Power Requirement, kw	NA	300	375
Power Cost, \$/day	NA	\$576	\$716
Dedicated Labor Cost, \$/day	NA	\$997	\$997
Demineralized Water Credit, \$/day	NA	(\$166)	(\$184)
Operating Cost, \$/day	NA	\$1,407	\$1,529
Amortization + Operating, \$/day	\$2,319	\$2,158	\$2,169

3.7.1.b Desert Plant - Disposal Costs

Based on the adjusted pan data for evaporation of 60 inches per year for the desert (0.33 acres per gpm of wastewater). If we assume that an additional 5 percent of wastewater will be generated that cannot be routed to the cooling tower because of water quality concerns, then plant wastewater generation will be approximately 61 gpm. Therefore, 20 acres of ponds are required to contain and evaporate the plant wastewater. At \$350,000 per acre, evaporation ponds would cost \$7,000,000.

A two acre evaporation pond would be required for evaporator concentrate at a cost of \$700,000. Evaporator and crystallizer costs are the same as those in the fresh water Central Valley scenario above. The results are summarized in Table 3-14.

An evaporator with 20 acres of evaporation ponds was selected on the assumption that the area required ponds would be limited (this of course would be a site specific constraint). Three-shift operation should be assigned to monitor cooling system chemistry, the side-stream softener and evaporator. A dedicated crew of five operators would be required to oversee the water systems for a daily cost of \$997 per day.

Table 3-14
Base Case - Fresh Water - Desert Inland Plant - Disposal Cost Summary

	Evap Pond Only	Evaporator & Evaporation Pond	Evaporator & Crystallizer
Evaporation Pond, acres	20	2	NA
Evaporator Feed, gpm	NA	61	61
Crystallizer Feed, gpm	NA	NA	6.1
Installed Cost	\$7,000,000	\$3,000,000	\$2,900,000
Amortization Cost, \$/day	\$1,546	\$662	\$640
Power Requirement, kw	NA	300	375
Power Cost, \$/day	NA	\$576	\$716
Dedicated Labor Cost, \$/day	NA	\$997	\$997
Demineralized Water Credit, \$/day	NA	(\$166)	(\$184)
Operating Cost, \$/day	NA	\$1,407	\$1,529
Amortization + Operating, \$/day	\$1,546	\$2,069	\$2,456

3.7.2 Base Case - Fresh Water - Coastal Plant

The cycles of concentration for the cooling tower was set at 9.4 - the maximum achievable without treatment (silica is the limiting constituent). Also, since this is a coastal setting, water conservation, i.e. higher cycles of concentration, is not critical. Parameters, such as calcium, magnesium and sulfate are moderately low and do not pose scaling problems. Refer to Table 3-15 for a summary of operating chemistry (as well as water quality criteria, chemical feed requirements, flow rates, etc.).

Cooling System Issues

At 9.4 cycles of concentration, the operating TDS of the cooling tower will be 2,000 mg/l. Admiralty brass type alloys can be employed for heat transfer surfaces. Carbon steel can also be used for all other components in the cooling system. Sodium hypochlorite (NaOCl) can be utilized for biological control. A residual of 1 mg/l of free available chlorine should be maintained twice per day for at least two hours per application. This should keep biological growth within control. The specialty chemical program should focus on corrosion control for carbon steel and copper alloy components.

Table 3-15
Cooling Water Chemistry - Fresh Water Case

Coastal Plant		Cycles of Concentration = 9.38		
	Units	Make-up	Acidified Make-up	Cooling Water
Na by Diff	mg/l _{CaCO3}	89	89	835
K	mg/l _{CaCO3}	1	1	9
Ca	mg/l _{CaCO3}	45	45	422
Mg	mg/l _{CaCO3}	3	3	29
HCO ₃	mg/l _{CaCO3}	75	21	200
CO ₃	mg/l _{CaCO3}	0	0	0
OH	mg/l _{CaCO3}	0	0	0
Cl	mg/l _{CaCO3}	31	31	291
SO ₄	mg/l _{CaCO3}	32	86	810
NO ₃	mg/l _{CaCO3}	ND	ND	ND
t-PO ₄	mg/l _{PO4}	ND	ND	ND
S	mg/l _S	ND	ND	ND
SiO ₂	mg/l _{SiO2}	16	16	150
B	mg/l _B	ND	ND	0
NH ₃	mg/l _N	ND	ND	0
pH		7	6.6	7.9
TDS	mg/l	222	207	1,947
TSS	mg/l	<1	<1	10-20
BOD	mg/l	ND	ND	(Note 3)
COD	mg/l	ND	ND	

Pct of Limit.....

CaxSO ₄	26%
MgxSiO ₂	6%
SiO ₂	100%
K _{SP} Ca ₃ (PO ₄) ₂ Saturation	NA
LSI - Target Range = -1 to +1	1.16
RSI - Target Range = +6 to +7	5.55

General Plant Data.....

Make-up, gpm	1,948
Blowdown, gpm	205
45% Sludge, tons/day	NA

Chemical Feed Requirement.....

Na ₂ CO ₃ , tons/day (1)	NA
Ca(OH) ₂ , tons/day (1)	NA
MgCl ₂ , tons/day (2)	NA
H ₂ SO ₄ , tons/day	0.63
Coagulant Aide, pounds/day	NA
Specialty Chemical, pounds/day	25 (10 mg/l in cooling tower)

Notes.....

1. Refer to Appendix B: Softener performance calculations - US Filter Technical Data Book, Section 56.
2. ND = non detectable.
3. BOD and COD not quantifiable in the cooling tower.

Operating Costs

Cooling tower chemicals and freshwater should cost \$4,615 per day. To maintain a residual of 1 mg/l of free available chlorine (OCI^{-1}) in 128,000 gpm of recirculating water for a total of four hours per day requires 559 pounds (dry basis) per day of sodium hypochlorite (1.5 times the calculated demand). Refer to Table 3-16 for an operating cost summary. Cooling system chemistry should be checked twice per shift to ensure that water quality parameters are within specification. Cooling tower blowdown should be automated (controlled continuously) based on circulating water conductivity (salinity).

Table 3-16
Base Case - Fresh Water - Coastal Plant - Treatment Cost Summary

Fresh Water, \$/day	\$4,305
98% Sulfuric Acid, \$/day	\$114
Specialty Chemical Formulation, \$/day	\$74
Sodium Hypochlorite, \$/day	\$196
Total Cooling Tower (basic chemicals)	\$4,689 (\$1.67/1000 gallons)

There is no water treatment equipment associated with this scenario.

3.8 Degraded and Fresh Water Comparisons

Operating data, treatment equipment requirements, chemical and power consumption, sludge production, dedicated labor and operating and capital costs developed for all the scenarios are summarized in Table 3-17. The rationale for waste treatment selection is discussed in the applicable sections of this report. At the bottom of the table is the daily operating cost which includes consumables, labor and amortization. The unit cost is the daily operating cost divided by cooling tower make-up. The last line of the table is the ratio of daily unit cost for degraded water to fresh water for same scenario, i.e. inland and coastal plants. *The summary shows that water costs associated with degraded water are at least 1.5 to 2.5 times the costs associated with fresh water at inland plants and 1.1 to 1.2 times that of fresh water at coastal plants (based on assumed water chemistries, Table 3-1, and the evaluation basis, Table 3-2).* These ranges could be broader/narrower depending on the quality of the water source. Generally speaking, the greater the TDS, hardness and silica of the degraded source water, the greater the ratio.

Lastly, the higher the TDS, the more sophisticated the materials of construction, e.g. 90-10 copper-nickel at TDS of 35,000 mg/l and titanium at TDS greater than 35,000 mg/l for the main condenser. Also, the presence of ammonia requires copper-nickel metallurgy and non-copper alloys (e.g. no admiralty brass). No costs were identified for these “metallurgical impacts”. As stated previously, only a few reclamation plants are nitrifying their effluent to remove ammonia.

Table 3-17
Comparison Summary - Degraded Water and Fresh Water (1)

	Degraded Water			Fresh Water		
	Case Study 1	Case Study 2	Case Study 3	Base Case 1	Base Case 2	Base Case 3
	Produced Water Central Valley	Agriculture Return Desert	Reclaimed Water Coast	Central Valley	Desert	Coast
Operating Data.....						
Cycles of Concentration	10.3	10.3	6.0	29.7	29.7	9.4
Degraded Water, gpm	1,928	964	2,088	NA	NA	NA
Fresh Water, gpm	NA	964	NA	1,801	1,801	1,948
Blowdown, gpm	185	185	345	58	58	205
Heat Exchanger Metal	90-10 Cu Ni	Titanium	90-10 Cu Ni	Copper Alloy	Copper Alloy	Copper Alloy
Treatment Equipment.....						
Make-up Softener, gpm	NA	1,928	2,088	NA	NA	NA
Side-Stream Softener, gpm	3,008	506	NA	290	290	NA
Evaporator, gpm	194	195	NA	61	61	NA
Crystallizer, gpm	19.5	NA	NA	NA	NA	NA
Evaporation Pond, acres	NA	6.4	NA	3.0	2.0	NA
Chemical Consumption.....						
98% Soda Ash, tons/day	4.63	14.07	0	0.47	0.47	NA
90% Lime, tons/day	1.77	5.11	2.90	0.41	0.41	NA
Magnesium Chloride, tons/day (2)	2.54	0	0	0.29	0.29	NA
Coagulant Aide, pounds/day	108	88	75	10	10	NA
98% Sulfuric Acid, tons/day	10.37	0	0.57	0.74	0.74	0.63
Chlorine Dioxide, pounds/day (2)	1,001	NA	1,001	NA	NA	NA
Sodium Hypochlorite, pounds/day (2)	NA	1,117	NA	559	559	559
Specialty Chemicals, pounds/day (2)	575	124	62	63	63	25
Other Operating Variables.....						
Sludge, tons/day	19.0	55.0	16.3	1.7	1.7	NA
Power, kwh/day	28,200	22,560	(Note 5)	7,200	7,200	(Note 5)
Connected Load, kw	1,175	940	(Note 5)	300	300	(Note 5)
Operating Costs.....						
Degraded Water, \$/day	\$426	\$213	\$2,307	NA	NA	NA
Fresh Water, \$/day	NA	\$2,130	NA	\$3,980	\$3,980	\$4,305
Treatment Chemicals, \$/day (5)	\$8,567	\$9,181	\$3,025	\$950	\$950	\$310
Power, \$/day	\$2,258	\$1,804	(Note 4)	\$576	\$576	(Note 4)
Demineralized Water Credit, \$/day	-\$587	-\$528	NA	-\$168	-\$168	NA
Dedicated labor, \$/day	\$997	\$997	NA	\$997	\$997	NA
Total Operating Cost, \$/day	\$11,661	\$13,797	\$5,332	\$6,335	\$6,335	\$4,615
Equipment Cost.....						
Water Treating Equipment	\$1,600,000	\$1,900,000	\$1,300,000	\$400,000	\$400,000	NA
Disposal Equipment	\$5,600,000	\$6,700,000	NA	\$3,400,000	\$3,000,000	NA
Total Equipment	\$7,200,000	\$8,600,000	\$1,300,000	\$3,800,000	\$3,400,000	NA
Amortization, \$/day	\$1,590	\$1,899	\$287	\$839	\$751	NA
Total Daily Cost	\$13,251	\$15,696	\$5,619	\$7,174	\$7,086	\$4,615
Daily Unit Cost, \$/1,000 gallons (6)	\$4.77	\$5.65	\$1.87	\$2.77	\$2.73	\$1.65
Cost Ratio - Degraded:Fresh	1.73	2.07	1.14			

Notes.....

1. 500 MW combined cycle plant.
2. 100% basis.
3. Refer to Table 3-2 for unit cost assumptions.
4. Minimal power requirement for water treatment and disposal - not calculated.
5. Includes sludge disposal.
6. Daily unit cost - operating cost per 1000 gallons of cooling tower make-up.

4

ENVIRONMENTAL IMPACTS

4.1 Introduction

Environmental impacts can issue from a variety of cooling tower streams and activities associated with the cooling circuit:

- Evaporation
- Drift
- Blowdown
- Waste streams from treatment processes associated with the cooling circuit
- Sludge generated from cooling system maintenance

All of these streams have the potential of transporting chemical constituents of concern and producing environmental impacts.

Depending on origin, degraded water can contain a variety of chemical constituents (refer to Section 2.3.1, Types of Degraded Water). Also, because cooling systems provide warm operating temperatures, ample surface area and low-flow environments, they can harbor and sustain a significant amount and variety of microbiological activity.

When degraded water is employed for make-up, cooling tower evaporation can contain gaseous contaminants in addition to water vapor, e.g. trace levels of volatile organic compounds. Depending on the source water, constituents of concern, such as trace levels of heavy metals and organic compounds, could also be found in the circulating cooling water. Since drift and blowdown are component streams of circulating water, they contain all of its chemical constituents. Biological pathogens such as *Legionella pneumophila*, which can thrive in cooling water systems and are transported via drift, pose a potential human health concern. Treatment processes, such as side-stream filtration and softening, evaporators and crystalizers, generate liquid, sludge and solid waste streams which are comprised of circulating water and its constituents - chemical compounds, particulate matter, biological material and treatment chemical byproducts. Lastly, sludge from cooling tower maintenance contains inorganic, organic and biological sediments generated by day-to-day operation.

This section discusses potential environmental impacts related to airborne and waterborne contaminants, water quality issues related to the disposal of blowdown and treatment process wastes, and safety as it relates to working in and around cooling towers.

4.2 Airborne and Waterborne Contaminants

Large cooling towers, such as those found at power plants, can move significant quantities of air. Air usually enters the tower through its side(s) and exits through the top. The air flow can carry particulate matter in the form of dust, soil, pollen, bacteria, vegetation, etc. Much of this material is literally scrubbed from the air stream as it moves through a highly-dispersed shower of circulating water. Therefore, a cooling tower collects most of the airborne particulate matter entering it. In addition to scrubbing ambient matter, the large quantities of air used for cooling can efficiently release volatile chemical compounds found in the source water as well as compounds generated by periodic halogenation for biological control.

Particulate material scrubbed from the air by recirculating water in a cooling tower settles in low-flow areas and forms sediment masses consisting of inorganic, organic and biological matter. Sediment in a medium of warm water provides an excellent environment for bacteria to colonize and reproduce. Conversely, bacteria already established on cooling tower surfaces, such as fill or packing, binds particulate matter into sediment masses. Sediment in fill sections of the cooling tower can overload tower structural members (in extreme cases, collapse the fill section or the entire tower) and cause air and water flow restrictions.

The possible suite of contaminants in cooling tower water utilizing degraded sources could be significant and, therefore, it is difficult to reasonably quantify environmental impacts or health risks. Also, many compounds found at barely-detectable concentrations may not have been identified as constituents of concern yet. As detection levels for compounds improve with time, more constituents of concern will be identified. In most cases, constituents of concern, e.g. volatile organic compounds, heavy metals, pesticides, etc., *will have to be removed to meet existing regulatory requirements before degraded water can be utilized for cooling*. The cooling tower will either emit the constituents in the air stream (possibly dispersed over long distances in populated areas) or concentrate and discharge constituents via drift or blowdown (possibly contaminating groundwater or surface water). In addition to chemical constituents of concern there are well-documented human health risks from the presence of *Legionella pneumophila* bacteria which can cause a sometimes-fatal respiratory infection.

4.2.1 Airborne

Some chemical compounds in degraded water will readily volatilize when exposed to the air flow of a cooling tower. Therefore, these compounds can be dispersed and carried over significant distances. As discussed in the Section 2.4, Rules and Regulations, *many volatile compounds are strictly regulated and will have to be removed from degraded water before it is fed to the cooling system*. Examples of volatile compounds are: chlorinated solvents (e.g. carbon tetrachloride, trichlorethane, methylene chloride, etc.), aromatic organic compounds (e.g. benzene, xylene, naphthalene, etc.), some pesticides (e.g. aldrin, dieldrin, lindane, etc.) and inorganic compounds such as hydrogen sulfide (as H_2S) and ammonia (as NH_3). Note that hydrogen sulfide and ammonia stripping are pH dependent and must be in their non-ionic forms to volatilize. (Hydrogen sulfide must be at a pH of less than 9 and ammonia at a pH of greater

than 7 to have their non-ionic forms present.) Of the pesticides cited, Aldrin is 37 times more volatile than ammonia (as NH_3) and dieldrin is 4 times more volatile. (Chidgopkar, 1996)

Volatile compounds can be generated when chlorine or bromine is utilized for cooling tower biological control. When halogens are added to the cooling water in the presence of natural organic matter (e.g. trace levels of byproducts of decomposing vegetation), trihalomethane (THM) compounds can be produced. Some examples of THMs are chloroform and bromoform. In addition to being very volatile, THMs are strictly regulated as health hazards. Degraded water sources prone to THM formation include municipal effluent, irrigation return, degraded water impacted by runoff from livestock or dairy operations, water used in oil field production (also known as produced water), etc. Fresh water can also be prone to THM formation if it carries naturally-occurring organic matter, e.g. lake or river water. Also, since the air flow to the tower can carry organic matter in the form of vegetation, THMs can be produced via this transport mechanism as well. Again, these compounds can be dispersed and carried over long distances.

THM generation in the cooling loop can be controlled by limiting halogenation, therefore, THM formation would only occur intermittently. Also, chlorine dioxide or ozone could be used for biological control if THM is a problem. Chlorine dioxide does not form THMs in the presence of precursors. Ozone does not directly produce THM either, however, in waters with significant bromide levels, the formation of bromoform has been observed. (Simpson, 1993) THM formation and fate in cooling systems is currently being studied in a joint effort funded by CEC and EPRI.

4.2.2 Cooling Tower Drift

All cooling towers experience drift to some degree. Drift is the entrained loss of small droplets of circulating water to the air flow (some droplets are small enough to be considered aerosols). Drift contains the chemical constituents, suspended material and bacteria found in the bulk circulating water. Using current technology, drift from cooling towers can be controlled to 0.002% to 0.006% of the circulating water rate depending on the drift elimination system selected. Some manufacturers are claiming drift rates as low as 0.0005%.

As an example (see below), a 500 MW combined cycle plant with a third of its power derived from steam generation will only generate 2.6 gpm of drift per day with a mist elimination rating of 0.002%.

Air Flow Rate	25,000,000 scfm
Evaporation Rate	1,750 gpm
Circulating Water Rate	128,000 gpm
Mist Eliminator Rating	0.002% (of the circulation rate)
Drift Rate	2.6 gpm (3,700 gallons per day)

As drift exits the tower, it can, depending on ambient meteorological conditions, evaporate quickly leaving an agglomeration of chemical constituents, suspended material and dehydrated biological matter dispersed in the air flow as dry particulate matter. The following constituents will be emitted as drift from the tower:

- Chemical constituents - concentrated source water constituents, trace levels of organic compounds, cooling tower treatment chemicals, etc. As the drift droplets evaporate, mineral salts will precipitate and many organic compounds such as pesticides will condense to form crystals.
- Suspended material - silt, scale, corrosion byproducts, etc.
- Biological matter - planktonic bacteria (free-moving organisms in the bulk cooling water), sessile bacteria (immobile organisms from biological sediments/deposits), organism metabolic byproducts, etc.

At the example drift rate of 2.56 gpm (discussed above), a cooling tower with a circulating water concentration of 10,000 mg/l (consisting of dissolved salts, suspended material and biological matter) will have a drift mass emission rate of 307 pounds per day of particulate matter.

Reisman, 2002 predicted that PM_{10} (particulate matter equal to or smaller than 10 microns) would comprise less than 10 percent of the drift mass from a cooling tower operating at a TDS level of 10,000 mg/l. Reisman used drift-droplet size-distribution data generated by EPRI at their test Houston facility in 1998. Assuming that most of the dissolved solids were comprised of sodium chloride (NaCl) and formed spheres when evaporated, the diameter of the particle formed could be calculated using the known density of NaCl. It is more likely that the particles form irregular shapes, making them larger than the predicted spherical diameters. EPA states that assuming all of the drift mass emissions are PM_{10} is very conservative and places its lowest confidence rating on this calculation known as AP-421 (EPA, 1995).

Drift is dispersed into the cooling tower air stream and travels (as droplets or de-watered particles) distances that are dependent on ambient conditions such as wind direction, wind speed, air temperature, relative humidity, etc. Drift can also carry legionella pneumophila which poses threats to human health (discussed next). Lastly, drift can also be a nuisance in the form of salt deposition in the vicinity of the cooling tower - this is especially true when the cooling tower is in an urban setting.

4.2.3 Legionella

Legionella pneumophila is the bacterium responsible for the well-documented outbreak of “Legionnaires’ Disease” in 1976. (Cooling Technology Institute (CTI), 2000 and American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE), 2000) Legionella can originate from a number of industrial and commercial sources including cooling towers and evaporative condensers. In the case of cooling towers, the pathway is drift - fine droplets or mist in the aerosol-size range carrying viable Legionella bacteria. OSHA estimates over 25,000 cases of the illness occur every year in the United States. More than 4,000 deaths are believed to occur, but only a fraction are reported. About 1,400 cases of Legionellosis are reported to the

Center for Disease Control (CDC) annually and about 500 are confirmed. Legionella is transmitted by breathing aerosol-sized droplets of water that contain the bacteria. For the infection to occur, aerosol droplets must be small enough (less than 2 µm in diameter) to travel to the deepest part of the lungs, the alveoli, where gas-exchange occurs. (ASHRAE, 2000) Infection can occur after an incubation period of two to ten days. Pneumophila is one of the 37 species of rod-shaped Legionella bacteria. However, the bacteria must be from one of the three serogroups of Legionella pneumophila that cause the infection (there are fourteen pneumophila serogroups (CTI 2000)). Symptoms include fever, chills, headache and muscle pain. A dry cough soon develops and most patients suffer with breathing difficulty. Some patients also develop vomiting and diarrhea. Treatment with antibiotics such as erythromycin is usually prescribed. Legionellosis can be fatal to at-risk individuals such as the elderly, smokers, individuals with chronic respiratory diseases, individuals with immuno-suppressed diseases, etc. It is estimated that Legionellosis is fatal to 10 to 20 percent of those who contract it and much higher for at-risk individuals.

Pontiac Fever is a less serious infection caused by Legionella. The symptoms of Pontiac Fever are similar to those of moderate to severe influenza - headache, fever, fatigue, joint pain, etc. The incubation period is usually one to two days and the illness passes in five to ten days. There is very little statistical data on this specific illness because it is rarely diagnosed correctly.

Transmission

Drift droplets containing Legionella bacteria must survive ambient conditions and not evaporate to be a threat to human health. Ambient air conditions that include low relative humidity will likely evaporate aerosol-sized drift droplets shortly after they exit the cooling tower. Larger drops exposed to air with low relative humidity could evaporate and shrink sufficiently to enter the alveoli. Conversely, under high-humidity conditions, drift aerosols could be carried for some distance, thus posing a potential health risk in urban areas or commercial/industrial parks. Drift poses more of a threat to individuals who work in the immediate vicinity of a cooling tower.

Monitoring

Various studies have shown that 40 to 60 percent of all cooling towers harbor Legionella bacteria. Cooling towers present ideal conditions for Legionella pneumophila to thrive - warm water and host environments such as bacterial slime (biofilms), sediments with bacteria, and protozoa (higher, unicellular life forms such as amoebas). Legionella readily reproduces inside these host environments. Legionella are difficult to directly control with standard biological treatment such as halogenation (chlorine or bromine), because they are shielded inside their host environment. Cooling towers that have been sampled to find “non-detectable levels of Legionella” can have thriving colonies days later. It is generally acknowledged that if a cooling tower can be kept relatively free of biofilm, sediment and protozoa, Legionella should not pose a threat because its host is removed. Certain constituents in degraded water such as organic nitrogen compounds are vital to aerobic heterotrophic bacteria such as Legionella because they require complex organic nitrogen and carbon compounds to survive. Therefore, using reclaimed

municipal effluent or irrigation runoff may encourage *Legionella* colonization in a cooling system.

Cooling towers should be monitored routinely for biofilm formation, sediment accumulation and the presence of planktonic protozoan hosts. Cooling tower fill, distribution deck, mist eliminators and the cooling tower basin should be inspected for obvious signs of biofilm and sediment. Circulating water should be sampled for protozoan hosts via dipslides, PetriFilm™ or other culturing techniques to quantify aerobic heterotrophic bacteria populations. There is usually a two-day wait for results using these methods. Also, a sample of circulating water can be inspected immediately for protozoa (assaying should only be done by a trained microscopist). There are a number of qualified labs that can provide this service (or it can be accomplished in conjunction with the specialty chemicals supplier). Lastly, culturing techniques (conducted by qualified testing labs) that quantify *Legionella* can take 10 to 14 days to obtain results. This period is considered too long and is not recommended. For immediate results, ATP biomonitoring (adenosine triphosphate, a natural metabolite) can also be used to quantify biological activity in circulating water and biofilm. ATP provides results in the form of relative light units (transmitted light) which can be correlated to biological activity.

Control

Cleaning programs usually involve keeping *Legionella* host environments under control. In a well maintained tower that is relatively free of biofilm, sediment and planktonic bacteria, continuous chlorination at low levels should keep *Legionella* in check. Before embarking on a *Legionella* control program, cooling tower operators are usually directed to inspect the tower for the presence and extent of biofilm and sediment and to sample the circulating water for protozoan hosts (as described above). In new cooling tower systems, design features can minimize sediment formation (e.g. avoiding piping dead legs) and biological control programs can be designed to deliver/maintain halogen residuals to the entire cooling loop. In one reference, side-stream filtration is recommended as a control option to remove planktonic hosts and inert matter that can be incorporated into sediment masses. (Meyer, 2000) Maintenance programs can be designed to incorporate routine inspections and cleaning procedures for sediment and biofilm. Lastly, record keeping, which documents daily halogen monitoring, occasional monitoring for *Legionella* and routine maintenance, can be instituted at the outset of operation as standard operating procedures.

For a system that is relatively free of biofilm, sediment and planktonic bacteria, routine treatment involves the continuous addition of halogens to maintain a hot-side residual of 0.5 to 1.0 mg/l of free available chlorine. As a minimum for a relatively clean system using fresh water for make-up, a halogen residual of 1 mg/l (throughout the cooling system) should be established for at least one hour per day. If cooling water pH is very alkaline (8.5 to 9.0), bromine should be used because it is more effective than chlorine at higher pH. Also, if ammonia is present in the water as would be found in reclaimed municipal effluent, bromine should be used as a disinfectant. Chlorine readily reacts with ammonia to form chloramines (it requires 8 to 13 mg/l of chlorine for every 1 mg/l of ammonia). Under these conditions, chlorine consumption could be quite high and controlling the halogen residual could be difficult. Chloramines have disinfectant properties

but act slowly (on an equivalence basis, 10 times the desired chlorine residual expressed as total residual chlorine is required when chloramines are present). Bromine also reacts with ammonia, but the reaction product is unstable and releases the bromine. For systems that are treated intermittently, non-oxidizing biocides may be required to supplement disinfection (treatment selection should be done in conjunction with a specialty chemicals supplier). Lastly, occasional hyperchlorination is recommended, especially for systems that are fed with reclaimed water or systems that have levels of planktonic bacteria exceeding 100,000 CFU/ml (colony forming units per milliliter). Hyperchlorination consists of maintaining a residual of 5 mg/l of free available chlorine for a period of six hours.

Cooling systems that discharge blowdown to regulated water bodies (ocean, rivers, lakes, etc.), will require dechlorination to meet federal, state and Regional Water Quality Control Board standards. Refer to Section 2.4, Rules and Regulations, Tables 2.4-2 and 2.4-3 for allowable halogen levels.

In older systems that have significant problems with biofilm and sediment, the cooling tower will have to be cleaned before a prevention program is put into place. Cleaning usually involves high doses of halogens (chlorine or bromine or both) and loosening agents, such as biodispersants and biodegredients, to dislodge biofilm and break apart sediments. Depending on the condition of the cooling tower, it could take repeated cleaning cycles (high dosing and circulation of biocides and biodispersants, purging and re-inspection) to reduce biofilm and sediment conditions. Also, sediments may have to be physically removed from the basin. Lastly, a maintenance programs should be instituted to incorporate routine inspections and cleaning procedures for sediment and biofilm along with record keeping.

Refer to Appendix A.1.2, Referenced Citations - Chapter 4, (citations 26 and 27) for hyperlink addresses to the full texts of Legionella guidelines and position papers prepared by the Cooling Technology Institute (CTI) and American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE).

4.3 Water Quality Issues Related to Blowdown

As discussed in Section 2.3, Chemical Constituents in Degraded Water, cooling towers concentrate the chemical constituents found in make-up water. Volatile constituents, as discussed above, readily leave the cooling tower via the air flow. Drift, although a relatively small stream, transports the constituents found in the circulating water. Blowdown, consists of all of the chemical and particulate mass that entered the cooling system less emission losses to air flow and drift. Blowdown consists primarily of non-volatile constituents, mineral salts and, depending on the source of degraded water, trace levels of heavy metals, pesticides, organic compounds, etc. The cooling system accumulates some particulate material, biological matter and mineral deposits that are not part of tower emissions. Depending on variables such as location, meteorological conditions, RWQCB Basin Plan goals, etc., blowdown can be discharged in a number of manners:

- Discharge untreated to a receiving body of water such as the ocean or a river

- Discharge untreated to an evaporation pond
- Treat and discharge to a receiving body of water
- Reduce in volume and discharged to an evaporation pond
- Reduce waste stream to dryness

In addition to the above waste streams for cooling tower blowdown, process wastes from side-stream filtration or side-stream softening are generated in some cooling systems. Also, periodic maintenance of cooling systems will generate sludge from accumulated sediment wastes.

4.3.1 Discharge Untreated to a Receiving Body of Water

Cooling tower blowdown (and other power plant waste streams) cannot be discharged directly to a receiving body of water unless it met federal, state and regional requirements as identified in Section 2.4, Rules and Regulations, Tables 2.4-2 and 2.4-3. At the state and federal level, discharge requirements for pH, free available chlorine, total chromium, zinc and 126 priority pollutants must be satisfied. In addition, discharge limits found in RWQCB Basin Plans must also be met.

4.3.2 Discharge Untreated to an Evaporation Pond

Ponds are typically employed in desert settings where there is sufficient net evaporation to economically justify this approach. For example, in the California high desert, one acre of pond area will evaporate a continuous stream of wastewater equivalent to 3 gpm. Evaporation is greater in the summer and much lower (possibly negative - rainfall accumulation) in the winter months. Typically, ponds appear to be drying up during the hottest summer months and accumulate water in the winter. RWQCBs have historically required evaporation ponds to be impervious (non-leaking) to protect underlying groundwater from the chemical constituents in cooling tower blowdown. Percolation ponds are not permitted for the disposal of cooling tower blowdown. The non-degradation policy of preserving existing groundwater quality is set forth in the Porter Cologne Act (this act also created the SWRCB and the RWQCBs). Refer to Section 2.4, Rules and Regulations. As long as an evaporation pond is impervious and hazardous materials (e.g. chlorinated solvents, heavy metals, etc.) are not being discharged, blowdown treatment is usually not mandated. The RWQCBs (as well as other agencies) also recognize that evaporation ponds will eventually contain all of the mineral salts, chemical constituents and sediment (from suspended material in the waste stream) disposed during the life of the plant. This sometimes raises concerns over possible impacts on migratory birds alighting on the ponds.

Since evaporation ponds are costly (\$350,000 to \$500,000 per acre), efforts are typically made to minimize wastewater generation by:

- Operating the cooling tower at high cycles of concentration to reduce cooling tower blowdown. Achievable high cycles of concentration are heavily dependent on source water quality and treatment (pre-treatment of source water and side-stream treatment of cooling

tower circulating water). Refer to Section 2.3.3.d, Treatment Requirements for Degraded Water.

- Water conservation and recycling to reduce wastewater from sources other than the cooling tower. Some candidate streams for recycle are plant area washdown water, ion-exchanger backwash and low-conductivity rinse water, boiler blowdown and RO reject (from fresh water treatment).

Water conservation should be instituted at all levels of plant operation - plant supervision, operators, maintenance workers, contractor workers, etc. to ensure sustained success. The cooling tower is critical to a recycle program because it usually is the recipient of many of the plant wastewater streams. Therefore, developing a recycling plan must take some forethought so streams that would otherwise damage cooling system components are not inadvertently released to the tower, e.g. very high/very low pH streams, concentrated ion-exchanger spent regenerant, oily wastewater or sediments from maintenance, etc.

Evaporation ponds must be constructed on relatively flat sites on soils that are competent and will not differentially slip. If a plant is being located in a hilly area, evaporation ponds are not practical because of the grading requirements and costs to produce an impervious flat-bottomed containment cell.

Lastly, evaporation ponds require monitoring throughout their service life. Pond inflow and level should be recorded daily and physical inspections (perimeter walks) should occur monthly. Groundwater monitoring is usually a requirement imposed by the local Regional Water Quality Control Board. These activities should be considered as operating costs for evaporation ponds.

4.3.3 Treat and Discharge to a Receiving Body of Water

As stated previously, the RWQCB will establish requirements for discharge of blowdown to a receiving body of water. Depending on source of water, there may be constituents of concern that must be removed (or reduced) to acquire a NPDES permit. For example, dischargers to San Francisco Bay must meet very stringent limits for copper (a possible trace metal in cooling tower blowdown). Depending on the source of water used for cooling, treatment could involve:

- Metals removal - precipitation or chelating ion exchange or both.
- Organic compounds removal - biological processes, ultraviolet destruction (UV), ozone oxidation, UV/ozone, activated carbon or a combination of these processes.
- Dehalogenation - the use of a reducing agent such as sodium bisulfite to destroy residual halogens.
- Possible pH adjustment.

Obtaining NPDES permits and the technical and cost unknowns associated with selecting/operating treatment processes are significant barriers to using degraded water for cooling tower make-up. Many projects have opted to eliminate the permitting process (even

with fresh water make-up for cooling) by utilizing “zero-discharge” water management strategies and equipment such as a combination of recycling, operating the cooling towers at high cycles of concentration and the use of evaporators and crystalizers to treat wastewater to dryness. The only water emitted from these plants (other than evaporated water and drift) is usually sanitary wastewater.

4.3.4 Reduce Volume and Discharge to an Evaporation Pond

This option is a variation of discharging untreated blowdown to an evaporation pond. This option would be used when:

- A plant does not have sufficient property to accommodate evaporation ponds.
- Ambient conditions do not support very large ponds, i.e. relatively low evaporation rate. In parts of the Central Valley, the annual net evaporation rate is approximately 2 gpm per acre as compared to 3 gpm in a desert setting. Therefore, if a power plant generates 150 gpm of wastewater (mostly cooling tower blowdown), a 50 acre evaporation pond would be required for the desert plant and a 75 acre pond for the plant in the Central Valley.
- The plant does not want to take on the long-term liability of large evaporation ponds that must meet a non-leaking standard.

Volume reduction is usually accomplished by a combination of plant water recycling, operating the cooling tower at higher cycles of concentration and, depending on the project, the use of an evaporator to significantly reduce the volume of wastewater from the plant. An evaporator can reduce overall plant wastewater volume by over 90 percent, but requires approximately 80 kwh of electric energy for every 1,000 gallons of water treated.

4.3.5 Reduce Waste Stream to Dryness

In this scenario, all plant wastewater is reduced to dryness leaving only the mineral salts, trace constituents of concern, chemicals used for water treatment, etc. that entered the plant for cooling and other process uses. This would eliminate the need for evaporation ponds and an NPDES permit since no liquid waste would be generated. This approach to managing wastewater is the most costly because it utilizes all of the control measures discussed above including crystallization. The solid waste would have to be removed from the site to a licensed disposal facility.

4.3.6 Treatment Process and Maintenance Wastes

In addition to evaporation, drift and blowdown, cooling systems can generate other process and waste streams. These include:

- Backwash waste from side-stream filtration
- Sludge from side-stream softening

- Maintenance waste from cooling tower maintenance

Side-stream filtration removes suspended material usually via pressurized media filters (sand is commonly used for a filtering media). Refer to Section 5.3.2a for a description of the filtration process and backwash procedures. When the filter is loaded (usually determined by pressure drop), it is taken from service and backwashed to dislodge and remove filtered material from the media. The backwash stream consists of the motive water (usually cooling tower make-up or any other particulate-free water) plus the dislodged suspended material. Suspended material can consist of corrosion products, scrubbed solid material from the air flow, mineral scale, filtered bacteria, etc. It usually is combined with cooling tower blowdown for disposal or it can be recycled if the receiving use can tolerate or remove the particulate matter.

Side-stream softening is typically used to reduce blowdown volume by removing hardness and silica from the circulating water to achieve higher cycles of concentration. Lime and soda ash are typically added to a reactor clarifier to treat “hot return water” from the cooling tower. Refer to Section 5.3.2b for a description of the reactor clarifier process. The warm water (105 to 115°F) facilitates silica removal to levels not achievable with cold water softening. The process generates sludge (3 to 7 percent solids by weight) which consists of precipitated mineral salts and suspended matter (and precipitated heavy metals if they are present in the circulating water). The sludge is usually dewatered to 20 to 40 percent solids prior to disposal (water from the sludge is returned to the feed of the reactor clarifier). Depending on the nature of the sludge (e.g. degraded water source with heavy metals), it may require special handling and disposal if it is determined to be a hazardous material. A hazardous designation is usually determined by testing for leachable metals (and if necessary, organic compounds). The pH of the treated effluent is usually adjusted before it is returned to the cooling tower.

Cooling tower maintenance can generate wastes in the form of dislodged sediment material, cleaning compounds (such as bio-dispersants) and wash-down water. Sediment can accumulate on fill, in low-flow piping, the cooling tower basin, etc. Cooling tower sediments, as discussed above, can contain mineral salts, heavy metals, silt, organic compounds, bacteria, etc.

4.4 Worker Safety

Worker safety issues can arise when working in and around cooling towers and related treatment equipment such as make-up and side-stream process treatment. Worker safety issues include (but are not limited to):

- Legionellosis and Pontiac Fever
- Exposure to untreated degraded water containing volatile compounds, pesticides, heavy metals, hydrogen sulfide, etc.
- Biological control chemicals such as chlorine and bromine compounds
- Specialty chemicals used for scale and corrosion control

- Chemicals (as well as waste streams) generated by water treatment equipment such as sulfuric acid, sodium hydroxide, hydrated lime, etc.
- Maintenance wastes such as biological sediments

Tools are available to assess Legionellosis and workplace hazards. In addition to the CTI guidelines and ASHRAE position paper, OSHA has an entire section of its technical manual dedicated to Legionnaire's Disease, Section III, Chapter 7. There is also a section on assessing and documenting Legionellosis cases, OSHA Appendix III:7-5, Water Treatment Protocols for Facilities That Have Experienced a Legionnaires' Outbreak.

Hazard and operability (HAZOP) studies are utilized by many corporations to evaluate potential workplace hazards. HAZOP studies can be implemented in the design phase of a project or after the plant has been in operation to identify and correct safety issues. Corrections can include physical modifications to the plant (such as safety shields for ion-exchange regeneration pumps) or procedural changes (such as improvements to communication and documentation during maintenance outages). Also, there are a significant number of HAZOP tools that are commercially available, e.g. software, training services, consultants, etc. to assist plant operators.

Lastly, other than exposure (dermal, oral or inhalation) to untreated degraded water containing volatile compounds, pesticides, heavy metals, hydrogen sulfide, etc., the above hazards are common in power plants. Treatment technologies discussed in Section 5.2, Pre-treatment Technologies - Environmental Constituents of Concern, are commonly used to treat and control constituents of concern in degraded water. Also, commercial equipment is available to handle and store untreated degraded water, e.g. double walled tanks. The chemicals used by these technologies, the waste streams that are generated and the physical equipment environment are no more hazardous than the equipment required for fresh water treatment, e.g. high-strength fuming acids, un-thickened treatment sludge, rotating equipment, high-voltage electric motors, etc.

5

COMMERCIALLY AVAILABLE TECHNOLOGY

5.1 Introduction

Treatment technologies that are commonly used to treat degraded water as well as technologies utilized for cooling tower make-up are identified in this section. The technologies discussed in this section are off-the-shelf, commercially available and widely used. Some applications for these technologies are not completely commercial - these are noted. Emerging technologies are discussed in the next section.

The technologies in this section are sorted into three areas:

- Pre-treatment technologies required to treat specific environmental problems in degraded water before using it for cooling
- Pre- and side-stream treatment technologies required to treat fresh or degraded water to prevent fouling and mineral scaling and/or to increase cycles of concentration
- Post-treatment technologies to minimize or eliminate cooling tower blowdown

Environmental problems in the context of this report are associated with chemical constituents encountered in the use of degraded water for cooling tower make-up, e.g. volatile organic compounds, pesticides, heavy metals, perchlorate, etc. There will also be situations when regulated chemical constituents, such as copper as a byproduct of corrosion, are discharged in cooling tower blowdown. Technologies used to treat environmental problems in cooling tower make-up are also applicable to blowdown treatment. Preventing fouling and mineral scaling and/or increasing cycles of concentration refers to removing chemical constituents that would impact heat transfer or impede cooling water flow, e.g. calcium, magnesium, ortho-phosphate, silica, etc.

Lastly, there are a significant number of treatment technologies and hybrid technologies that are commercially available. This section highlights many of the common approaches to treating degraded and fresh water.

5.2 Pre-Treatment Technologies - Environmental Constituents of Concern

Degraded water sources potentially could contain a variety of chemical constituents that must be removed prior to use as cooling tower make-up. Refer to Section 2.4, Environmental Concerns, for a general discussion of degraded water regulatory issues. Treatment approaches can be

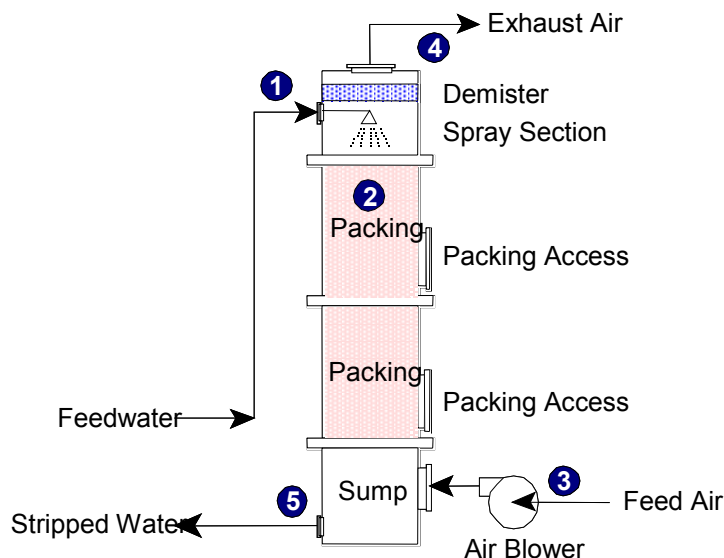
organized into a number of categories depending on the constituents to be removed. Refer to Table 2-7 for a general summary of treatment options and the constituents that are influenced by each technology. Treatment categories discussed in this section are:

- Air stripping followed by vapor-phase granular activated carbon (GAC) for the removal of regulated volatile organic compounds, THMs and some pesticides
- Air stripping followed by vapor-phase thermal oxidation for the removal of regulated volatile organic compounds, THMs and some pesticides
- Liquid-phase GAC for the removal of regulated volatile and non-volatile organic compounds (including pesticides) and incidental removal of some BOD and some COD
- Aerobic biological treatment for the removal of organic compounds and ammonia and incidental removal of BOD and COD.
- Anaerobic biological treatment for the removal of many organic compounds, AsO_4^{-3} , CrO_4^{-2} , SeO_4^{-2} , SeO_3^{-2} and ClO_4^{-1} (arsenate, chromate, selenate, selenite and perchlorate) and incidental removal of BOD, COD, possibly NO_3^{-1} , etc.
- Strong-base anion ion exchange for the removal of AsO_4^{-3} , CrO_4^{-2} , SeO_4^{-2} , SeO_3^{-2} and ClO_4^{-1} and incidental removal of PO_4^{-3} (ionic species), NO_3^{-1} and F^{-1}
- Chelating ion exchange for the removal of Cu, Ni, Cd, Cr^{+3} , etc.
- Precipitation for the removal of Cu, Ni, Cd, Cr^{+3} , AsO_4^{-3} , CrO_4^{-2} , SeO_3^{-2} and incidental removal of PO_4^{-3} and F^{-1} (under certain conditions)

Note, “incidental removal” as cited above refers to the removal of constituents that are not of environmental concern but are also removed (incidental constituents can also affect plant performance). Each of the treatment approaches discussed in this section will remove most, but not all of the constituents of concern. Complete removal is usually designated as “removed to non-detectable levels”. Process descriptions follow.

5.2.1 Air Stripping

Generally speaking, volatile organic compounds readily vaporize in air if a water/air interface is established. Air strippers are designed to break water into droplets which film over packing in the presence of a counter-flowing air stream and efficiently transfer the volatile compounds to the air. Refer to Figure 5-1 for a process description. Air strippers are utilized when volatile organic concentrations are too high to economically be removed by liquid phase carbon, i.e. liquid-phase carbon, which is less efficient than vapor-phase carbon, would require more frequent GAC change-outs. Air strippers are routinely designed to remove 99+ percent of volatile components entering the tower. Usually the stripper is sized (volume of packing and air flow) based on the volatile component with the lowest vapor pressure or Henry’s Constant. (Chidgopkar, 1996) Many counties in California (especially those in air quality non-attainment areas) have mass emission limits on the volatile compounds released from air strippers.



Information provided by Recovery Equipment Supply

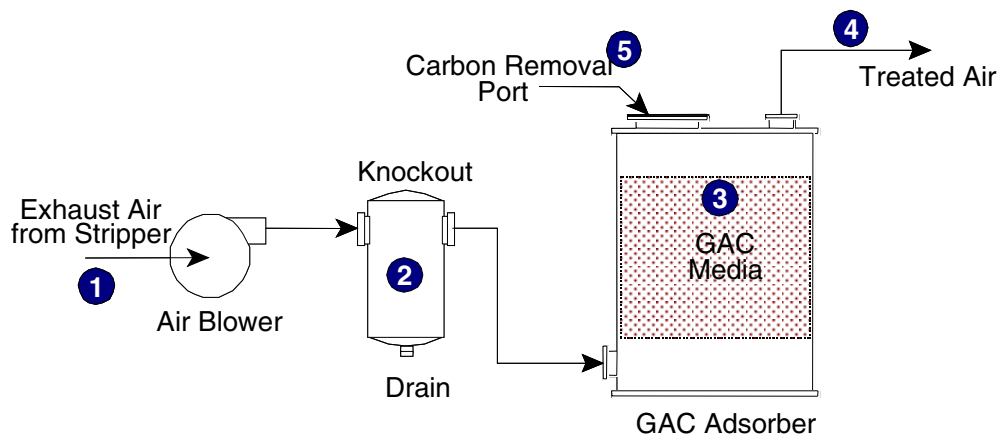
Process Description

1. Water containing volatile compounds is supplied to the top of the air stripping tower where it is sprayed above packing.
2. The falling water films over the packing creating air-water contact that allows the compounds to volatilize into the air.
3. Air is supplied by a blower at the base of the stripping tower.
4. Exhaust air exits the tower through a demister which traps entrained droplets of water. Depending on the volatile loading, the air may be treated further with vapor-phase GAC or thermal oxidation. Refer to Figures 5-2 and 5-3.
5. Stripped water collects in a sump at the base of the tower where it is pumped for further use.

Figure 5-1
Air Stripper

5.2.1.1 Air Stripping followed by Vapor-Phase GAC

Most air strippers utilize vapor phase GAC or thermal oxidation (discussed next) to capture stripped organic compounds. In vapor-phase GAC, stripper exhaust air is fed to a vessel containing carbon media. Refer to Figure 5-2 for a process description. The carbon, which is highly porous, readily adsorbs the organic compounds by trapping them in microscopic pore spaces. When the GAC is spent, the vessel is removed from service. Small vessels are replaced, e.g. drums and canister-type vessels. The media in permanent large systems is evacuated and replaced with fresh media. California has a network of providers that routinely replace GAC cannisters and media. GAC can be regenerated in place. Steam is typically used to drive trapped organic molecules from GAC pores. However, the condensed steam contains the all volatile compounds removed by the carbon which then have to be properly disposed or destroyed. It is mainly for this reason that on-site regeneration is not typically done for GAC systems treating volatile-organic chemicals.



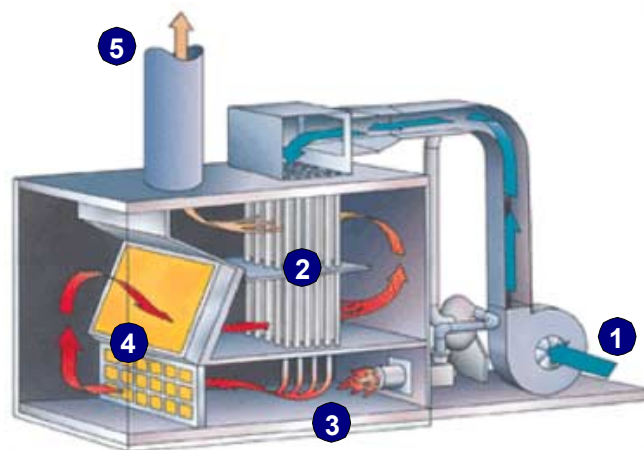
Process Description

1. Exhaust air from the stripper enters a blower to push it through the GAC adsorber.
2. The air then passes through a knockout to remove condensed water vapor. This step helps to preserve carbon efficiency.
3. Air enters the bottom of the adsorber where it passes through the GAC media. Volatile organic compounds are captured by the GAC.
4. Treated air exits the adsorber from the top of the cannister or vessel.
5. When the carbon is spent, it is removed from the vessel and replaced with fresh GAC.

Figure 5-2
GAC Vapor-Phase Adsorber

5.2.1.2 Air Stripping followed by Vapor-Phase Thermal Oxidation

This alternative utilizes thermal oxidation (incineration) to convert air-stripped organic compounds to combustion byproducts. There are a number of thermal oxidizer types and configurations. (Anguil, 1998) Each is suited to economically treat a range of organic concentrations and stripper exhaust flows. Also, there are a number of service providers that supply fully-automated portable and permanent systems. Refer to Figure 5-3 for a process description of one type of commonly used oxidizer - catalytic thermal oxidizer. The oxidizer converts carbon-based organic compounds to water and carbon dioxide via controlled combustion. Natural gas is burned using a blend of stripper exhaust air and ambient air. Some thermal units treat chlorinated organic compounds which are oxidized to form water, carbon dioxide and hydrogen chloride (anhydrous hydrochloric acid). Thermal oxidation of chlorinated organic compounds requires a scrubber to neutralize the acid. Typically, many system owners select vapor-phase carbon when chlorinated organic compounds are present in stripper exhaust because it is usually less costly and much less complex than a thermal oxidizing unit outfitted with a scrubber.



Information provided by Anguil Environmental Systems

Process Description

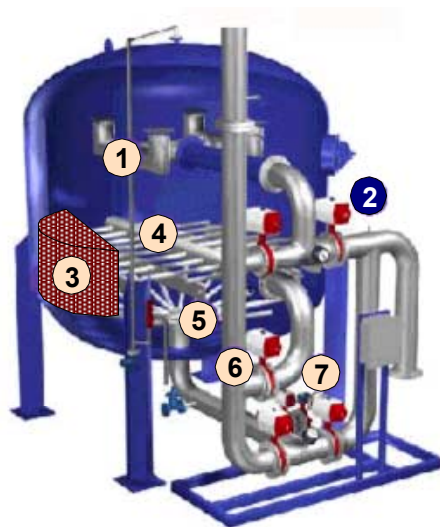
1. During operation, exhaust air from the stripper is drawn into the system fan.
2. The air is then preheated through the tube side of the heat exchanger.
3. After exiting the heat exchanger, the preheated air passes the burner, where the organic laden air is raised to operating temperature.
4. As the laden air passes through the catalyst, an exothermic (heat releasing) reaction takes place. The catalyst facilitates the reactions and enables combustion to occur at lower temperatures. The organic compounds are converted to carbon dioxide and water vapor. The hot treated air then passes through the shell side of the heat exchanger where the energy released by the conversion reactions passes to the incoming air to be treated. In this manner, the heat exchanger minimizes fuel consumption.
5. The treated air exits the oxidizer through the stack.

Figure 5-3
Catalytic Thermal Oxidizer

5.2.2 Liquid-Phase GAC

As stated previously, if the concentrations of volatile organic compounds are low enough, liquid-phase GAC is typically selected over air stripping. If non-volatile organic compounds are present (e.g. most pesticides), air stripping will not remove these compounds and liquid-phase GAC will be required. Also, some contaminated groundwater sources require a combination of gas-phase and liquid-phase organic treatment because they contain a mix of volatile and non-volatile compounds. In these situations, volatile compounds are first removed with air stripping and vapor-phase GAC, and the remaining organic compounds are removed with liquid phase GAC. Lastly, if the concentrations of non-volatile organic compounds are high, liquid-phase GAC may not be economical. At this point, biological treatment may be required (discussed next). Refer to Figure 5-4 for a process description of liquid-phase GAC. Because the media-filled liquid-phase GAC vessel is treating a liquid stream, it will also act as a filter by trapping suspended material, e.g. a single-media sand filter. As suspended material builds on/within the

GAC media, it must be backwashed periodically to prevent high pressure drop across the bed and a reduction of service flow. Therefore, liquid-phase GAC vessels are designed and operated in the same manner as media pressure filters. Valves are arranged to admit and treat degraded water in the service mode and to raise the bed during backwash to release trapped suspended material. When liquid-phase GAC media becomes spent, it will be removed and replaced with fresh media in much the same manner as vapor-phase media.



Information provided by Glegg Water Conditioning

Process Description

1. Water to be filtered or treated enters through the service inlet distributor. The distributor directs the water downwards to the media where particulate matter or organic constituents (GAC media only) are removed.
2. Depending on the application, media can be selected for filtration (e.g., sand or sand and anthracite) or organic removal (GAC). The media is located below the inlet lateral.
3. The treated water is collected in the hub and lateral underdrain assembly. This collector is also used to admit backwash flow uniformly to the media bed.
4. Treated water exits the vessel through the service outlet valve.
5. When the pressure drop across the media bed or the service volume reaches a preset level, the run is terminated and the filter enters the backwash mode. The backwash inlet valve is opened to start the cleaning cycle. Backwash flows up through the vessel and lifts the bed to dislodge particles that have been trapped on the media.
6. Some filters have sub-surface inlet distributors (4 to 6 inches below the top of the media) that break up the particulate mass that accumulates on the top of the bed before full-bed backwash is initiated. This step enhances particulate removal especially in filters where particulate loading is heavy.
7. Backwash exits through the waste valve to plant drain.

Figure 5-4
Vertical Pressure GAC, Media Filter

5.2.3 Biological Treatment

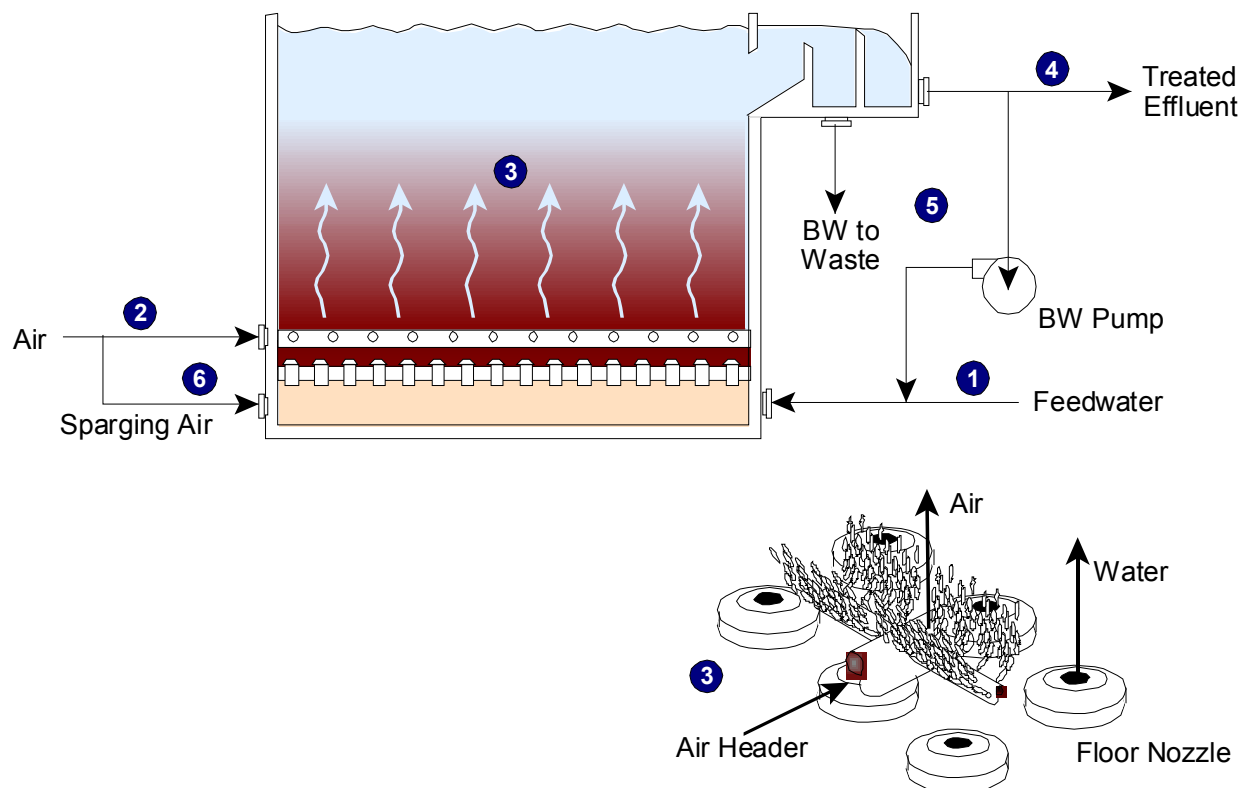
There are two biological treatment techniques that can be utilized to treat degraded water - aerobic treatment (in the presence of oxygen) and anaerobic treatment (in the absence of oxygen). Organic compounds, BOD and COD are converted to carbon dioxide and water and ammonia is converted to NO_3 (nitrification) with aerobic biological treatment. Chemically-bound oxygen compounds such as phosphate, nitrate, chromate, arsenate, etc. are reduced to their elemental forms with anaerobic biological treatment.

5.2.3.1 Aerobic Biological Treatment

Aerobic treatment utilizes aerobic bacteria to metabolize organic compounds. Oxygen is introduced in the presence of water and organic material (some degraded water sources may require supplemental carbonaceous feed, such as methanol, to support bacterial respiration). The microbes resident in the biological reactor metabolize the organic material and oxygen to sustain life and reproduce and generate byproducts of carbon dioxide, metabolized mineral compounds (such as sulfates, phosphates and nitrates), polysaccharide excretions (which bind suspended material) and sludge in the form of flocculated masses of inert suspended material and live and expired microbes. There are a number of aerobic biological reactor configurations, e.g. activated sludge (feed air is used to fluidize the microbes and sludge), trickling filter (water falls through a fixed-film biological reactor in the presence of air) and specialized reactors such the Biofor aerobic biological filter. (Peladan, 1998) The Biofor process has been used commercially to remove ammonia (nitrification) from secondarily treated municipal effluent to be used for cooling tower make-up. Specialized bacteria known as nitrosomonas and nitrobacters are utilized to metabolize ammonia and convert it to nitrite then nitrate. A fine clay media (fluidized in the process) is used as a substrate for the bacteria. The Biofor process also clarifies/filters the nitrified water. (Corbin, 1998) Refer to Figure 5-5 for a description of the Biofor process. Depending on feed concentrations, aerobic biological treatment is an effective way to remove ammonia from water.

5.2.3.2 Anaerobic Biological Treatment

Anaerobic treatment utilizes anaerobic bacteria and fixed or bound oxygen to metabolize organic and inorganic compounds such as SO_4^{-2} , NO_3^{-1} and PO_4^{-3} . Anaerobic reactors operate under starved oxygen conditions, requiring the microorganisms to utilize chemically-bound oxygen to survive. Anaerobic biological treatment has also been used to remove SeO_3^{-2} (selenite), SeO_4^{-2} (selenate), CrO_4^{-2} and AsO_4^{-3} from water, but most of the work in this area has been experimental. Most studies have focused on finding and sustaining bacteria that are tolerant to these mineral salts since they are toxic to most bacteria. Biological sludge containing metals, such as selenium, chromium and arsenic removed by biological treatment, has been a problem because many landfills will not accept this waste material. Anaerobic treatment has also been studied for the removal of ClO_4^{-1} from water. A large plant is currently under construction in central California to treat perchlorate-contaminated groundwater.



Process Description

1. Water containing ammonia and organic compounds is supplied to the bottom compartment of the biological reactor. Water enters the reactor through evenly spaced nozzles.
2. Air also enters in the bottom of the reactor co-current with water to be treated. Air is dispersed as fine bubbles evenly into the water to be treated with a network of sparging laterals.
3. Inert media is fluidized by the flow of aerated water. The media is covered with a thin film of bacteria which easily degrades organic compounds and ammonia. In addition to biological degradation, the media effectively filters the water as it rises through the reactor.
4. Treated and filtered water exits the reactor over a weir.
5. When reactor solids build to a pre-determined level (usually after 24 to 48 hours), the reactor is backwashed. Backwash pumps supply treated water to lift excess suspended material.
6. Sparging air is utilized to supply oxygen to inactive BIOFOR modules to maintain bacteria viability.

Figure 5-5
BIOFOR Aerobic Biological Filter

5.2.4 Ion Exchange

This section describes two types of ion exchange that can be used to treat degraded water:

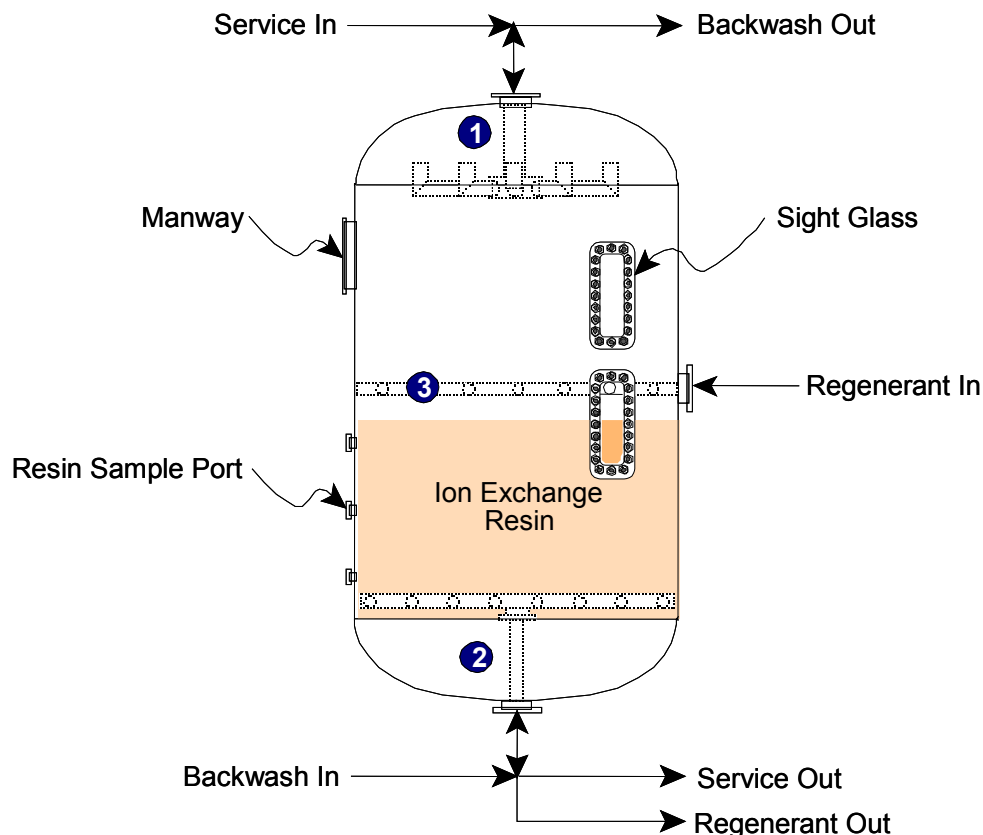
- Strong-base ion exchange for the removal of AsO_4^{-3} , CrO_4^{-2} , SeO_4^{-2} , SeO_3^{-2} and ClO_4^{-1} along with incidental removal of PO_4^{-3} (ionic species), NO_3^{-1} and F^{-1}
- Chelating resin for the removal of Cu^{+2} , Ni^{+2} , Cd^{+2} , Zn^{+2} , etc. along with incidental removal of Fe^{+2} , Ca^{+2} and Mg^{+2}

In the ion exchange process, constituent ions of concern are “exchanged” for environmentally acceptable ions. The predominant form of ion exchange delivery is the resin bead. Powdered and liquid ion exchange systems are also available (for certain applications). Typically, resin beads vary in size from 16 to 45 mesh. The resin is usually housed in a pressurized vessel to a minimum depth of 30 inches. Refer to Figure 5-6 for a description of the ion exchange process. On a molecular level, beads are sponge-like porous structures comprised of strands of polymers that have functional exchange sites implanted throughout. Ion exchange occurs on the functional sites. Pore space within the bead is filled with water - the bead is approximately 50 percent water by weight. The water allows ions to move throughout the bead.

There are numerous types of commercially available ion exchange resins - strong-acid, weak-acid, chelating, strong-base, weak-base, etc. One US manufacture sells over 400 types of ion exchange resins and related functional products. Strong-acid, weak-acid and chelating refer to cation exchange resins. Strong-base and weak-base refer to anionic resins. Strong and weak refer to “salt splitting” characteristics, i.e. the overall ability to exchange ions. For example, strong base refers to the ability to exchange virtually all negatively-charged ions (with some exceptions), even weakly dissociated salts such as silicic acid (expressed as $\text{HSiO}(\text{OH})_3$, commonly known as silica). Weak-base and weak-acid resins have limited salt-splitting capability, but usually have more ion exchange capacity. Chelating resins have a high affinity for transition (heavy) metals.

In ion exchange, the constituent ions of concern exchange with the ions attached to the functional site within the bead. A very stable bond (ionic bond - an electron exchange) is formed between the ion and the functional site. Chelating resin beads utilize a different mechanism - the metal⁺² ion is exchanged for two Na^{+1} ions captured and held in place by two or three “chemical arms” (e.g. acetic acid branches, $-\text{CH}_2\text{COO}^{-1}$). The branches hold the metal ion using covalent bonding (less stable bond - shared electrons rather than exchanged electrons).

When the resin in the ion exchange vessel reaches its capacity to exchange, it is regenerated. Refer again to Figure 5-6. Depending on the resin and the application, strong-acid and weak-acid resin are usually regenerated in the hydrogen or sodium form, chelating resin in the sodium form and strong-base and weak-base in the hydroxide or chloride form. Form refers to the exchangeable ion that is placed on the functional site during regeneration. In degraded water treatment for cooling tower make-up, the sodium and chloride form would be utilized. The hydrogen and hydroxide forms would create low and high (respectively) pH problems causing severe corrosion or scaling.



Process Description

1. In the service mode, water enters the top of the vessel and the flow is evenly distributed. As the water moves through the vessel it passes through the ion exchange resin where (depending on the type of resin) anions or cations of concern are exchanged for desired ions, e.g. chloride or sodium ions.
2. Treated water is collected at the base of the bed and exits to service.
3. When the ion exchange resin becomes fully loaded, the vessel is taken out of service. The resin is first backwashed by running water through the bottom of the bed to lift it and dislodge particulate matter (in the same manner as filters). Then a pre-determined amount of regenerant is passed through the middle distributor (acid, caustic or brine or a combination of these). After the regenerant has passed, the bed is rinsed slowly to evenly displace the regenerant and then fast to rinse the remaining regenerant from the bed. The ion exchanger is then ready for service.

Figure 5-6
Ion Exchange

Unlike the above technologies, where constituents of concern are either destroyed or removed from the site for destruction by others, ion exchange concentrates the compounds removed in the form of a much smaller volume of regeneration wastewater. For example, if an ion exchange system treats 100,000 gallons of water with a feed concentration of $0.5 \text{ mg/l CrO}_4^{-2}$ and generates 5,000 gallons of wastewater during regeneration, the concentration of CrO_4^{-2} in the spent regenerant would be 10 mg/l ($0.5 \text{ mg/l CrO}_4 \times \text{Vol}_{\text{Treated}} \div \text{Vol}_{\text{Regen}}$). Therefore, regeneration

wastewater will require further treatment. In some cases, ion exchange might be used as a pre-concentrating technology. The waste stream cited in the above example could be treated with a much smaller CrO_4^{-2} reduction/precipitation system (process discussed later). Of note, there is one commercial ion exchange system (which utilizes continuously moving columns of fine-mesh ion exchange resin) that reportedly generates a waste stream that is less than one percent of the treated volume. (Jennings, 2000)

Lastly, ion exchange resin is not selective. In the above example, the resin will exchange sulfate, bicarbonate and nitrate in addition to CrO_4^{-2} . Typically, the full capacity of the resin is not realized for target ions.

5.2.4.1 Strong-Anion Ion Exchange

Strong-base ion exchange can be used to treat contaminated groundwater to remove anionic target constituents, e.g. AsO_4^{-3} , CrO_4^{-2} , SeO_4^{-2} , SeO_3^{-2} and ClO_4^{-1} . (Jennings, 2000 and Catts, 1997) Strong-base resin in this service would be regenerated in the chloride form. As stated above, if the strong-base resin treating groundwater were regenerated in the hydroxide form, the pH of the treated water would be elevated with severe precipitation of background salts, e.g. CaCO_3 and $\text{Mg}(\text{OH})_2$. When the resin becomes loaded (most of its ion exchange capacity is used), a 7 to 10 percent solution of sodium chloride is passed through the resin bed to re-exchange the anions removed during service. The pH of feed to the strong-base ion exchanger, when in service, may have to be adjusted to completely ionize constituents to be removed. In addition to ion exchange, strong-base resin has some organic removal capability. Organic compounds are not removed by ion exchange, they are trapped in the molecular matrix of the resin bead - most (but not all) of the organics are removed during regeneration.

5.2.4.2 Chelating Ion Exchange

Commercial chelating ion exchanges can be used to treat degraded water containing divalent heavy metals, e.g. Cu^{+2} , Ni^{+2} , Cd^{+2} , Zn^{+2} , etc. In addition to removing heavy metals, the resin will also remove common divalent metals, e.g. Fe^{+2} , Ca^{+2} and Mg^{+2} . Therefore, the full capacity of the resin is not realized for heavy metal removal. Chelating resin is regenerated by first passing a five percent solution of hydrochloric acid (or sulfuric acid) followed by a five percent solution of sodium hydroxide. As discussed above, chelating ion exchange is a concentrating treatment, therefore, post treatment will likely be required to treat the concentrated, smaller volume of spent regenerant.

5.2.5 Precipitation

Precipitation can be used to remove a variety of cationic and anionic constituents of concern, e.g. Cu^{+2} , Ni^{+2} , Cd^{+2} , Cr^{+3} , AsO_4^{-3} , CrO_4^{-2} , SeO_3^{-2} as well as incidental removal of PO_4^{-3} and F^{-1} (under certain conditions). Two types of precipitation processes will be discussed:

- Removal of Cu^{+2} , Ni^{+2} , Cd^{+2} , Cr^{+3} , etc. by direct precipitation

- Removal of AsO_4^{-3} and SeO_3^{-2} by co-precipitation

CrO_4^{-2} (Chrome VI) requires a pre-treatment step of reduction to Cr^{+3} (Chrome III) before it can be removed from solution.

5.2.5.1 Direct Precipitation

Transition metals such as Cu^{+2} , Ni^{+2} , Cd^{+2} , Cr^{+3} , etc. are easily removed from solution with the addition of OH^- (by the addition of sodium hydroxide, NaOH) or S^{-2} (by the addition of sodium sulfide, Na_2S). Metal hydroxide precipitation requires good chemical feed control because some target metals precipitate in a narrow pH range (Amer, 1998) as shown below:

Metal	pH _{Min}	pH _{Max}
Cu^{+2}	7.0	7.5
Ni^{+2}	9.0	11.0
Cd^{+2}	9.0	11.0
Cr^{+3}	6.5	7.0

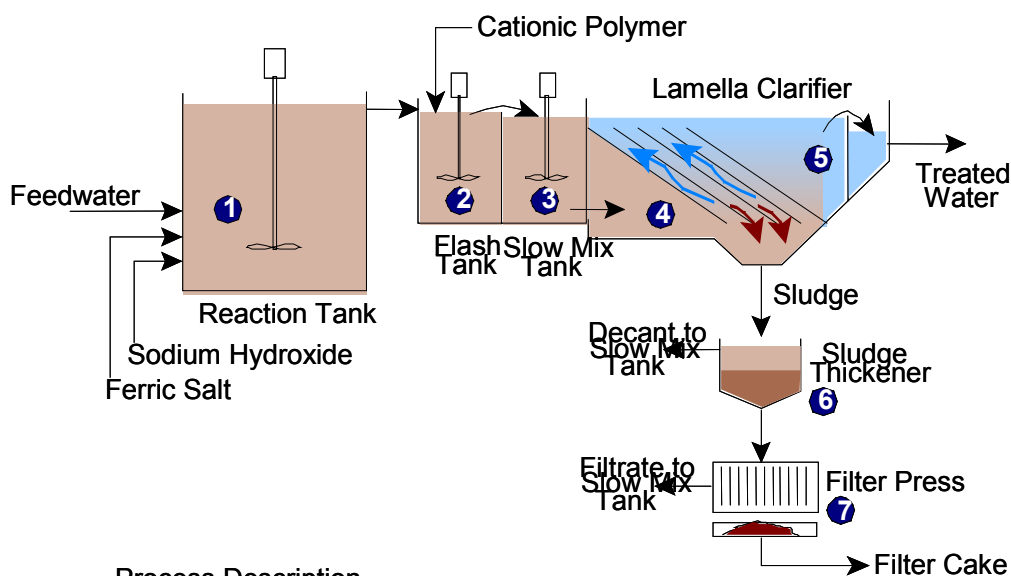
Also, because removal pH ranges vary, it would not be possible, for example, to simultaneously remove Cu^{+2} and Ni^{+2} , i.e. each metal is clearly out of the other's optimal removal range for pH. In these cases, two separate precipitation stages would be required. Less costly hydrated lime (calcium hydroxide) could be used as a substitute for sodium hydroxide but, depending on the alkalinity of the degraded water, lime can generate 5 to 10 times the sludge (or more). Refer to Figure 5-7 for a process description. As stated previously, ion exchange may be required to concentrate constituents to effect desired removal in a precipitation process, because, if starting concentrations of constituents to be removed are very low, precipitation may not achieve desired treatment concentrations.

Sulfide precipitation can provide better effluent quality in some cases. Sulfide is usually fed to a slight excess, creating an additional constituent to be removed from the water. Sulfide sludge can also generate toxic hydrogen sulfide gas (H_2S) if accidentally exposed to acid, and some landfills refuse to accept sulfide sludge. This precipitation approach is being used less frequently for the above reasons.

5.2.5.2 Co-Precipitation

Co-precipitation is becoming a popular approach for the removal of AsO_4^{-3} and SeO_3^{-2} . (Chritodos, 2000) It is less sophisticated and less costly than ion exchange and more of a proven technology and easier to control than anaerobic biological treatment. As stated previously though, ion exchange may be required to concentrate constituents to effect desired removal in a precipitation process. In co-precipitation a ferric salt (FeCl_3 or $\text{Fe}_2(\text{SO}_4)_3$ or a ferrous salt that is oxidized in the reaction tank) is used to generate a highly charged precipitate that attracts and

entraps AsO_4^{-3} and SeO_3^{-2} ions. Refer again to Figure 5-7 for a process description. Depending on the operating pH, this approach will also precipitate cationic heavy metals that are present in the same degraded water source being treated.



Process Description

1. Water to be treated enters the Reaction Tank, where it is mixed with sodium hydroxide and a ferric salt. The tank is sized to allow the components to completely mix and react. Heavy metals form their insoluble hydroxide products and mingle and attach to the highly charged, relatively dense ferric hydroxide precipitate.
2. Cationic polymer is added to the Flash Tank to encourage finely dispersed crystals to agglomerate and form a floc (an agglomeration of precipitated crystals).
3. The Slow Mix Tank further encourages the formation of the floc.
4. The water/floc mixture enters the Lamella Clarifier below the inclined-plate section. The mixture is forced to rise through the plates. The abrupt change in direction, encourages separation of the the flocculated mass from the water. The floc collects on the plates as the water rises. As the floc mass grows on the plates it dewater slightly and becomes more dense. The floc mass migrates slowly to the bottom edge of the plates and falls to the sludge sump.
5. After the water exits the inclined plate section, it overflows a weir where it leaves the clarifier.
6. The sludge (densified floc mass), is further thickened in a Sludge Thickener. The decant from thickening is returned to the Slow Mix Tank.
7. The thickened sludge is dewater in a Filter Press. Filtrate is returned to the Slow Mix Tank. Dried filter cake is disposed.

Figure 5-7
Precipitation, Co-Precipitation

5.2.5.3 Hazardous Waste Characterization of Sludge

Title 22 of the California Code of Regulations provides guidelines for determining the hazardous waste characterization of sludges (among many other possible types of waste). Depending on constituent concentrations in the sludge generated by precipitation or co-precipitation, there are prescribed tests to determine the concentration of the inorganic and organic contaminants in the

sludge as well as a wet extraction testing to determine leachable constituents. If the sludge is determined to be hazardous, it will require proper documentation (manifests) and disposal.

5.3 Pre-, Side-Stream, Post Treatment Technologies

Pre-treatment and side-stream treatment technologies discussed in this section, depending on water quality, apply to both fresh and degraded water. These performance-related technologies are typically employed to protect heat transfer surfaces (especially the main condenser) and minimize suspended material from fouling cooling tower fill. To achieve these performance goals, treatment equipment must be capable of:

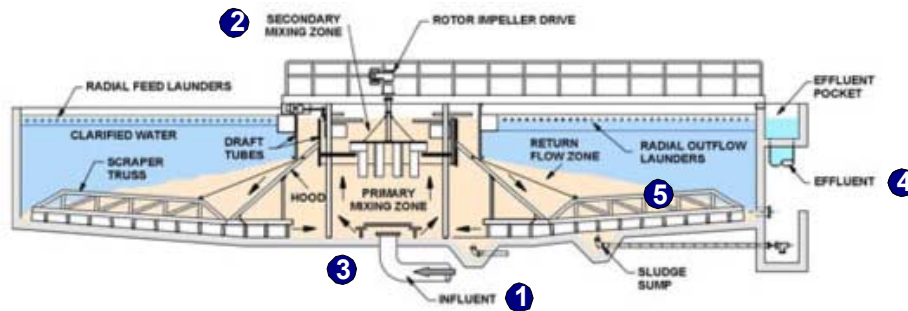
- Lowering the mineral content of make-up and/or circulating water, e.g. calcium, magnesium, alkalinity, phosphate, silica, etc.
- Removing suspended material from make-up and/or circulating water

Post treatment in the form of blowdown reduction is usually considered for inland plants where disposal options are limited to evaporation ponds.

Refer to Table 2-6 for a summary of treatment approaches and the constituents that are influenced by each technology.

5.3.1 Pre-Treatment

For large cooling systems, lime or lime/soda softening is typically used for make-up treatment. Lime/soda softening is designed primarily to remove hardness (calcium, Ca^{+2} and magnesium, Mg^{+2}) and carbonate alkalinity (CO_2 , HCO_3^{+1} and CO_3^{+2}). Other constituents such as phosphate, fluoride and suspended matter are also removed in make-up softening. Hardness removal (depending on source water chemistry) will usually allow the cooling tower to operate at higher cycles of concentration. There may be some incidental removal of silica (SiO_2) as well. Refer to Figure 5-8 for a process description. Lime (CaO), which has to be slaked (hydrolyzed) to $\text{Ca}(\text{OH})_2$ and soda ash (Na_2CO_3) are fed as a slurry to the softener. Depending on the relative amounts of calcium, magnesium and alkalinity and desired effluent chemistry, lime may only be required for treatment. Hardness and alkalinity criteria are usually selected based on limiting cycles of concentration. Refer to Section 2.3.3a, Cycles of Concentration. For example, in desert settings, cooling systems operating at high cycles of concentration are preferred to limit blowdown volume and wastewater treatment (i.e. evaporation ponds, evaporator/crystallizers, etc.). If the source water in this example has high hardness which limits cycles of concentration, then make-up softening should be considered.



Information provided by Infilco Degremont

Process Description

1. The reactor clarifier is divided into four zones. Raw water enters the primary reaction zone where it mixes it with lime, soda ash and cationic polymer (to enhance floc formation). In this type of reactor clarifier, sludge is kept in suspension - this enhances silica removal.
2. The combination of returned sludge flow and effective mixing by the rotor-impeller prevents solids from settling on the basin floor. The flow is pumped from the primary zone to the secondary zone where continued sludge contact allows the treatment reactions to approach equilibrium.
3. When the slurry leaves the secondary zone it is discharged downward between the inner and outer draft tubes into the returned flow zone. The flow moves downward and outward along the sloping hood, and onto the surface of the sludge pool.
4. The treated water separates from the downward moving mass and is displaced upward into the clarified water zone where it is collected.
5. Sludge is moved to the waste sludge sumps by the scrapers and drawn off intermittently. Sludge thickening and dewatering is not shown (refer to Figure 5-7)

Figure 5-8
Reactor Clarifier

Refer to Tables 2-5 and 3-1 for examples of screening source waters to determine limiting water quality criteria. Make-up softening has been used for the past 60 years in numerous cooling systems. When evaluating the need for make-up softening, the source water should be screened to determine which components limit cycles of concentration. A methodology for evaluating the need for make-up softeners follows:

- Identify the range of constituent feed concentrations (minimum, average and maximum) identified in Table 2-3. If maximum conditions occurs infrequently, then average conditions could be used. On the other hand, if maximum conditions occur frequently, then maximum conditions should be used. Lastly, if only a few data points exist, use the maximum known concentration plus 15 to 20 percent to account for possible unknowns.
- Determine the design cycles of concentration for the cooling system, N_{Design} . For an inland plant, high cycles of concentration (10 to 15 or more) may be required to minimize wastewater disposal. For a coastal plant with an outfall, five cycles of concentration may suffice.

- Refer to Table 3-1 to calculate limiting cycles of concentration for the source water for for $\text{Ca} \times \text{SO}_4$ product, $\text{Mg} \times \text{SiO}_2$ product, SiO_2 , etc. If any of the calculated cycles of concentration for a specific criteria are less than N_{Design} , then make-up softening may be necessary. For example, if $N_{\text{CaSO}_4} = 7.8$ and $N_{\text{Design}} = 10$, then calcium must be removed with softening to achieve 10 cycles of concentration (softening will not remove sulfate, SO_4).
- Make-up softening will remove calcium, magnesium, iron, aluminum, some silica, alkalinity, phosphate and fluoride.
- Refer to Appendix C for procedures to predict the removal of calcium, magnesium and alkalinity with lime or lime/soda softening. After the water to be treated is classified (e.g. form of alkalinity, non-carbonate hardness, etc. as described in Appendix C), reactor clarifier performance can be selected and the requirements for lime and soda ash can be determined. (Water and Wastewater Treatment Data Book) This procedure will also be referenced for side-stream softening (discussed later).
- Refer to Figure 5-11 to predict silica removal for make-up (cold water) lime or lime/soda softening. (Applebaum, 1968)
- Refer again to Table 3-1 to re-calculate limiting cycles of concentration for the source water for $\text{Ca} \times \text{SO}_4$ product, $\text{Mg} \times \text{SiO}_2$ product, SiO_2 , etc. assuming make-up softening. When evaluating phosphate and fluoride limitations, assume they are removed with make-up softening usually to acceptable levels. Calcium and magnesium product water from the softener can be modified to some degree to further reduce these constituents.
- If calcium, magnesium and/or silica are still limiting, side-stream softening (alone or in combination with make-up softening) may be required. *Refer to 5.3.2b, Side-Stream Lime/Soda Softening to continue the analysis.*

This process operates at a relatively high pH, 9.5 to 11.0, depending on feedwater hardness and alkalinity and the desired treatment levels for each hardness constituent. Lime/soda softening will also remove suspended matter in the feedwater. Phosphate constituents, which are converted to PO_4^{-3} at operating pH, and fluoride readily react with calcium. Also, many heavy metals are removed in the process via precipitation and co-precipitation.

Sludge production could be significant depending on the amount of hardness to be removed. Sludge which is usually generated at 3 to 7 percent solids (by weight) is usually thickened and dewatered to 35 to 45 percent solids to reduce its volume. As described above in 5.2.5c, Hazardous Characterization of Sludge, depending on the constituents removed during softening (e.g. heavy metals), the sludge may require analysis to evaluate whether it is a hazardous waste prior to disposal.

5.3.2 Side-Stream Treatment

There are two areas of side-stream treatment discussed in this section - filtration and softening. Side-stream filtration is used to control suspended matter in the cooling system. Side-stream

softening is employed to control scaling compounds (Ca^{+2} , Mg^{+2} and SiO_2) and to achieve higher cycles of concentration.

5.3.2.a Side-Stream Filtration

Side-stream filtration is employed when suspended matter concentrations in the source water are high enough to exceed the limits set forth in Table 2-3 at planned cycles of concentration in the cooling system. Suspended matter is also known as total suspended solids, TSS. Recall, film fill cannot tolerate high suspended solids because of its potential to plug, especially in the presence of bacterial films. Refer to Figure 5-4 for a description of the process (the vessel design can also be used for liquid-phase GAC).

Side-stream filters are usually located on hot side of the cooling circuit to take advantage of the pressurized water coming from the main condenser (i.e. no pumping is required). A stream of water is drawn from the return line and fed to the filters. Filtered water is returned to the cooling tower basin. Many side-stream filters are sized on a rule-of-thumb basis, i.e. typically at one percent of circulating water flow. The filters can also be sized on a mass flow basis as follows:

Note, this analysis is not necessary if make-up or side stream softening planned for cooling system treatment because either process will remove TSS.

- Identify the range of feed TSS conditions (minimum, average and maximum) and select a design point. Many designers will evaluate average and maximum conditions to calculate side-stream filter capacity. If maximum conditions occurs infrequently, then average conditions could be used to calculate filter capacity. On the other hand, if maximum conditions occur frequently, then maximum conditions should be used.
- Determine if side-stream filters are required. Calculate the cycles of concentration for the cooling tower, N , without considering TSS. Refer to Section 2.3.3a, Cycles of Concentration, for calculation methodology and Table 3-1. Then calculate the cycles based on TSS. If TSS is limiting, then side-stream filters are required. Refer to Table 2-3 for TSS water quality criteria.

$$N_{TSS} = \frac{300}{C_{TSS,MU}} \quad (\text{cooling tower with open fill or packing}) \quad (1)$$

$$N_{TSS} = \frac{100}{C_{TSS,MU}} \quad (\text{cooling tower with film fill}) \quad (2)$$

Filters are required if $N_{TSS} < N$

Where:

N_{TSS}	Cycles of concentration based on Total Suspended Solids
$C_{TSS,MU}$	Total Suspended Solids in the cooling tower make-up
N	Cycles of concentration <u>without considering TSS</u>

- If side-stream filters are required, the following mass flow analysis should be conducted to calculate the capacity of the filters:

$$MU = E + D + BD \quad (3)$$

$$BD = \frac{E}{N - 1} - D \quad (4)$$

$$F = \frac{C_{MU,TSS} MU - C_{CT,TSS} (D + BD)}{C_{CT,TSS}} \quad (5)$$

Where:	MU	Cooling tower make-up rate, gpm
	E	Evaporation rate, gpm
	D	Drift rate, gpm
	BD	Blowdown rate, gpm
	N	Cycles of conc <u>without considering TSS</u> (refer to Section 2.3.3a)
	F	Side-stream filtration rate, gpm
	$C_{MU,TSS}$	TSS in cooling tower make-up, mg/l
	$C_{CT,TSS}$	300 mg/l TSS for a cooling tower with open fill or packing
	$C_{CT,TSS}$	100 mg/l TSS for a cooling tower with film fill

Filters are usually sized so there are one or more units in operation and one on standby. When a filter is taken off line to be backwashed, the idle unit can be put immediately into service. Backwash is required when the pressure drop across a filter reaches a pre-set limit (usually 10 to 15 psi). Backwash is an automated procedure and is usually conducted without operator attention.

5.3.2.b Side-Stream Lime/Soda Softening

Source water with high levels of silica (or silica and magnesium) can severely limit cooling tower cycles of concentration. Refer again to Table 2-3 for cooling tower water quality criteria. For example, if a degraded water source has a silica (SiO_2) concentration of 40 mg/l, the cooling tower would be limited to 3.8 cycles of concentration. Recall that 5 cycles of concentration is considered a reasonable minimum value. At 3.8 cycles of concentration, 40 percent more blowdown will be generated than a tower operated at 5 cycles. Make-up softening will remove some SiO_2 , however, the amount of removal is usually not significant. Refer again to Appendix C for lime or lime/soda softening operating criteria to achieve different levels of performance. Silica removal depends on the amount of magnesium removed as $\text{Mg}(\text{OH})_2$ and the temperature of the water. $\text{Mg}(\text{OH})_2$ floc (agglomerated particles of precipitate) is highly charged and silica is attracted to and adsorbs onto its surface. Other variables like recirculating sludge can be controlled to maintain high floc density (and therefore floc surface area) within the reactor clarifier to enhance silica removal. The advantage of side-stream softening is that the water is warm, usually 105 to 115°F. Refer to Figure 5-12 to predict silica removal for warm-water softening. A side-stream of hot return (from the condenser) is fed to the reactor clarifier. Hot

return is typically 50 to 70°F warmer than source water. At elevated temperature, silica removal is dramatically improved. (Matson, 1979, Weis, 1980 and Knight, 1981) Also, hardness removal reactions are more complete.

Refer again to Figure 5-8 for a process description. Side-stream softening has been used for the past 30 years in a number of cooling systems. It is not used frequently because the process can be difficult to control especially with water sources that have variable constituent chemistry. Also, the control of cycles of concentration can be difficult in cooling systems.

As with make-up softening, hydrolyzed lime and soda ash (Na_2CO_3) are fed as a slurry to the softener. Depending on the relative amounts of calcium, magnesium and alkalinity and desired effluent chemistry, lime may only be required for treatment.

If the make-up softening analysis shows that hardness and silica removal criteria are still not achieved to meet the design cycles of concentration for the cooling tower, N_{Design} , then side-stream softening with or without make-up softening will be required. Note, if after evaluating make-up and side-stream softening, the water quality criteria are still not met and/or the size of the side-stream treatment equipment seem unnecessarily large, *then the basis for N_{Design} should be re-evaluated to allow for closure of the analysis.*

The size of the side-stream softener can be estimated as follows:

$$MU = E + D + BD \quad (3)$$

$$BD = \frac{E}{N_{\text{Design}} - 1} - D \quad (6)$$

$$SS = \frac{C_{\text{MU},\text{SiO}_2} MU - C_{\text{CT},\text{SiO}_2} (D + BD)}{C_{\text{CT},\text{SiO}_2} - C_{\text{SS},\text{SiO}_2}} \quad (7)$$

Where:	MU	Cooling tower make-up rate, gpm
	E	Evaporation rate, gpm
	D	Drift rate, gpm
	BD	Blowdown rate, gpm
	N_{design}	Design cycles of concentration
	SS	Side-stream softener capacity, gpm
	$C_{\text{MU},\text{SiO}_2}$	Make-up silica concentration, mg/l _{SiO2}
	$C_{\text{CT},\text{SiO}_2}$	Cooling tower silica criteria, mg/l _{SiO2} (from Table 2-3)
	$C_{\text{SS},\text{SiO}_2}$	Side-stream softener effluent silica, mg/l _{SiO2}

In the above equation, $C_{\text{SS},\text{SiO}_2}$ can be varied to adjust the size of the side-stream softener. $C_{\text{SS},\text{SiO}_2}$ can be adjusted by the degree of magnesium removal in the softener. Refer to Appendix C for a relationship between precipitated magnesium and determining the value of $C_{\text{SS},\text{SiO}_2}$. In some cases, magnesium is added to the softener in the form of magnesium chloride (MgCl_2) to create

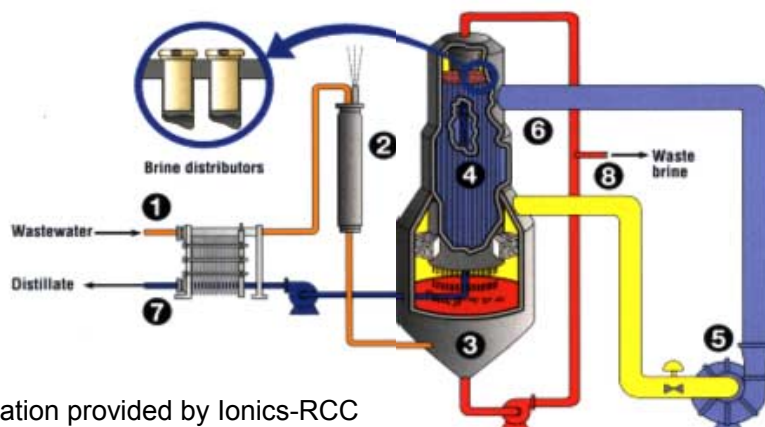
more floc when insufficient magnesium is present. Recall that surface of $\text{Mg}(\text{OH})_2$ floc is highly charged and adsorbs silica. Sludge recirculation is also used to enhance silica removal by supplying floc back to the reaction area. Lastly, magnesium can be removed by make-up softening, therefore, when performing this analysis, this should be taken into consideration when evaluating operating scenarios that involve both make-up and side-stream softening.

5.3.3 Post-Treatment

Post treatment in the form of blowdown reduction is usually considered for inland plants where disposal options are limited to evaporation ponds. Plants that have outfalls to receiving bodies of water or that can discharge to municipal wastewater treatment plants usually operate at relatively low cycles of concentration and post treatment (other than de-chlorination or pH adjustment) is not considered. Inland plants strive to operate at high cycles of concentration to minimize blowdown volume (as well as other wastewater generation) since all wastewater must eventually be stored on site as a liquid in evaporation ponds or hauled off the site as salt cake. Many evaporators are installed in conjunction with make-up or side-stream softening to minimize blowdown and thus the evaporator (and crystallizer) size. Lastly, evaporators are employed in areas where there is not enough physical space for evaporation ponds or evaporation ponds are too large because of insufficient evaporation (e.g. the Central Valley of California). There are two forms of post-treatment that are being utilized in California, evaporators and evaporator-crystallizer process combinations.

5.3.3.a Evaporators

Evaporators are used to concentrate power plant wastewater to a fraction of its original volume, usually to 10 percent or less. Most evaporators in this service utilize vapor recompression to drive the process. Refer to Figure 5-9 for a process description. Vapor recompression evaporation has been used to treat power plant wastewater for the past 30 years so there is a significant amount of operating experience. Because evaporators are costly, efforts are made to minimize plant wastewater via operating the cooling tower at elevated cycles of concentration, recycling wastewater streams within the plant, being water conscious in discretionary water use (e.g. wash down water), etc. Evaporators (and crystallizers) are significant power consumers as well. The evaporator produces a high quality distillate which is often re-used (with minimal treatment) for boiler feedwater or for gas turbine NO_x control. Evaporator concentrate can be very saline (100,000 to 200,000 mg/l or more). Concentrate, sometimes known as brine, is disposed to evaporation ponds or further treated to dryness via crystallization. In addition to soluble salts, brine can contain precipitated mineral salts as well as other constituents found in the cooling water.



Information provided by Ionics-RCC

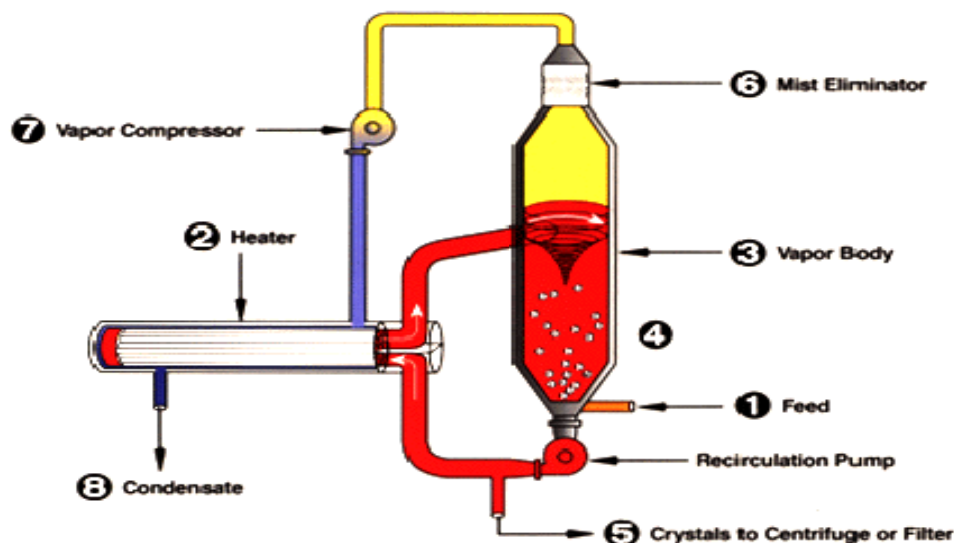
Process Description

1. Wastewater enters a feed tank (not shown) where pH is adjusted between 5.0 and 6.0 to convert alkalinity to CO₂. The acidified water is then passed through a heat exchanger that raises its temperature.
2. The wastewater passes through a deaerator which removes CO₂ and other non-condensable gasses such as oxygen.
3. Hot wastewater combines with brine slurry in the sump. Slurry is constantly recirculated from the sump to a floodbox at the top of the bundle of the heat transfer tubes. Specially designed brine distributors (tube inserts) encourage uniform film formation.
4. Some of the brine evaporates as it flows in a falling film down the heat transfer tubes and back into the sump.
5. The vapor passes through mist eliminators and enters the vapor compressor. Compressed vapor flows to the outside of the heat transfer tubes.
6. Heat from the compressed vapor is transferred to the cooler falling brine falling inside the tubes, causing some of the brine to evaporate. As the compressed vapor releases heat, it condenses as distillate.
7. The distillate is pumped through the heat exchanger, where it releases heat to the incoming feedwater.
8. A small amount of recirculated brine is released from the sump to control brine density.

Figure 5-9
Evaporator

5.3.3.b Evaporators and Crystallizers

If evaporation ponds cannot be used, then evaporator brine can be concentrated to dryness. There are some plants that either do have the space for ponds or the evaporation rate is not economically significant so a crystallizer is employed. There are a number of process configurations, e.g. forced-circulation vapor compression crystallizers and spray dryers. Refer to Figure 5-10 for a process description of a forced-circulation vapor compression crystallizer. The advantage of a crystallizer is that the wastewater stream is converted to salt cake. The salt, which requires toxicity analysis, see 5.2.5c, Hazardous Waste Characterization of Sludge, can be disposed offsite.



Information provided by Ionics-RCC

Process Description

1. Wastewater enters the bottom of the crystallizer. Forced-circulation vapor compression crystallizer is shown.
2. Wastewater joins the recirculating brine and is pumped to the shell and tube heat exchanger (feed heater). Because the tubes are flooded and under pressure, the brine will not boil (this prevent tube scaling).
3. The circulating brine enters the crystallizer vapor body tangentially, where it swirls into a vortex. A small amount of brine evaporates.
4. As water is evaporated from the brine, crystals form .
5. Most of the brine is recirculated back to the heater. A small stream from the recirculating loop is sent to a centrifuge or filter to separate crystals from the brine.
6. The vapor from evaporation passes through a mist eliminator.
7. The vapor is compressed. The compressed vapor heats the recirculating brine as it condenses on the shell side of the heater. (Plant steam is sometimes used for this purpose).
8. Condensate is collected for reuse in the plant.

Figure 5-10
Crystallizer

5.4 Treatment Costs

Costs for technologies discussed in Section 5.3, Pre-, Side-Stream, Post-Treatment Technologies are presented in this section. Refer to Figure 5-13 for a presentation of installed costs. (Dalan, 2000 and Trussell, 1980)

Costs were not estimated for remediation technologies described in Section 5.2, Pre-Treatment Technologies - Environmental Constituents of Concern. This analysis is not within of the scope of this report because of the process uncertainties created by the very large range of constituents to be removed and the treatment variables associated with desired or regulated effluent concentrations. For example, depending on the volatile constituent to be removed by air stripping (highly volatile versus moderately volatile) and their degree of removal, *the system could consist of one, two, three or more towers in series or in parallel (or a combination of both) for a given flow rate.* This extreme variability also applies to liquid- and vapor-phase GAC systems, thermal oxidation systems, biological treatment systems, etc.

Installed costs for equipment includes the purchased cost of the equipment as well as process and installation engineering, materials of construction, construction labor and equipment, administrative costs and contingency. The costs should be considered “order of magnitude” with an accuracy range of +50%/-35%, i.e. the installed cost could be 50 percent greater than presented in Figure 5-13 or 35 percent less. Variations in estimates to actual costs are affected by site conditions, regional labor costs, project duration and start up (e.g. work slows during the colder months), dramatic variations in construction material costs, unforeseen complications (e.g. pilings needed for foundations), etc. Equipment costs from dated references were revised using the Marshall & Swift Equipment Cost Index.

Operating costs are presented in Figure 5-14 for make-up and side-stream reactor clarifiers which use lime and soda ash to soften water (silica is also removed). Refer to Figure 5-8 for a process description. The operating costs which include lime, soda ash and polymer, cover a large range of feedwater hardness and alkalinity. Note, the upper edge of the cost envelope is for 500 mg/l_{CaCO₃} of feed alkalinity and the lower edge for 100 mg/l_{CaCO₃}. Lines within the envelope identify 100 mg/l_{CaCO₃} gradations of alkalinity. A similar graph was developed for sludge generation - refer to Figure 5-15. Dewatered sludge generation (40 percent solids by weight) can be determined by locating feedwater hardness and alkalinity on the envelope. Costs were not developed for sludge disposal because they vary greatly based on plant location.

Side-stream filtration operating costs are relatively small. Some filters are fed a coagulant aide (polymer). The operating cost for polymer (feed concentration of 1 to 2 mg/l and a polymer cost of \$2.00 per pound) would amount to \$0.016 to \$0.032 per 1,000 gallons of feedwater. Refer to Figure 5-4 for a process description.

The predominant cost for vapor compression evaporators is electrical power. Refer to Figure 5-9 for a process description. The evaporator will consume 70 to 100 kwh per 1,000 gallons of distillate depending on feedwater chemistry. The operating cost for evaporation (95 percent distillate recovery and power at \$0.08 per kwh) would be \$5.90 to \$8.40 per 1,000 gallons of feedwater.

Forced-recirculation crystallizers, which can also use vapor compression, operate at roughly twice the operating cost of evaporators - \$12 to \$17 per 1,000 gallons of feed water. Refer to Figure 5-10 for a process description.

Labor costs were not included in any of the above operating expenses since power plants usually apportion labor throughout the facility. If full-time operation (5 full-time staff to cover three shifts, 365 days per year) were dedicated to a complex/integrated water and wastewater treatment system, full-time operator coverage would cost \$1,000 per day at \$35 per hour (base pay plus benefits).

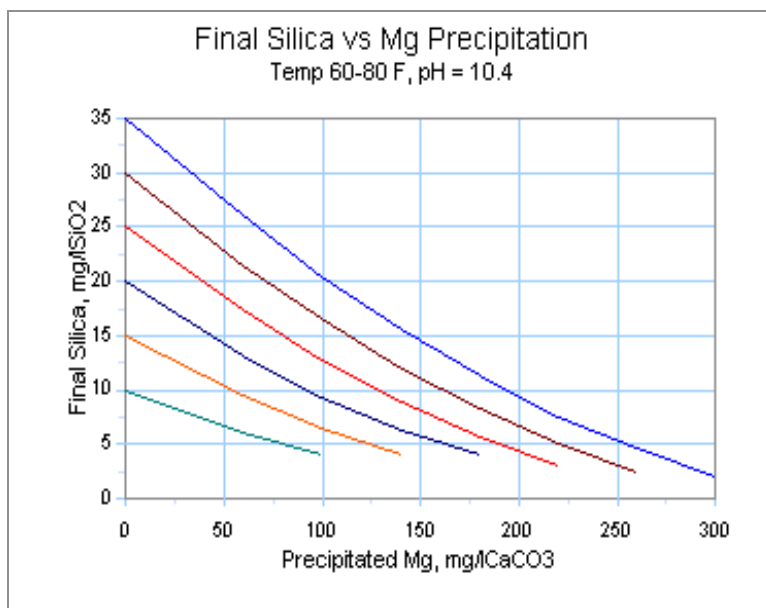


Figure 5-11
Final Silica vs Mg Precipitation (Temp 60-80°F, pH = 10.4)

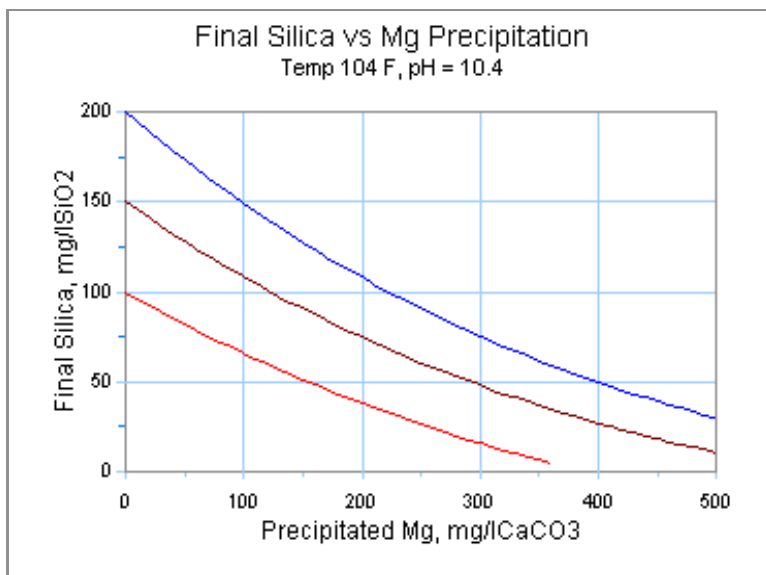


Figure 5-12
Final Silica vs Mg Precipitation (Temp 104°F, pH = 10.4)

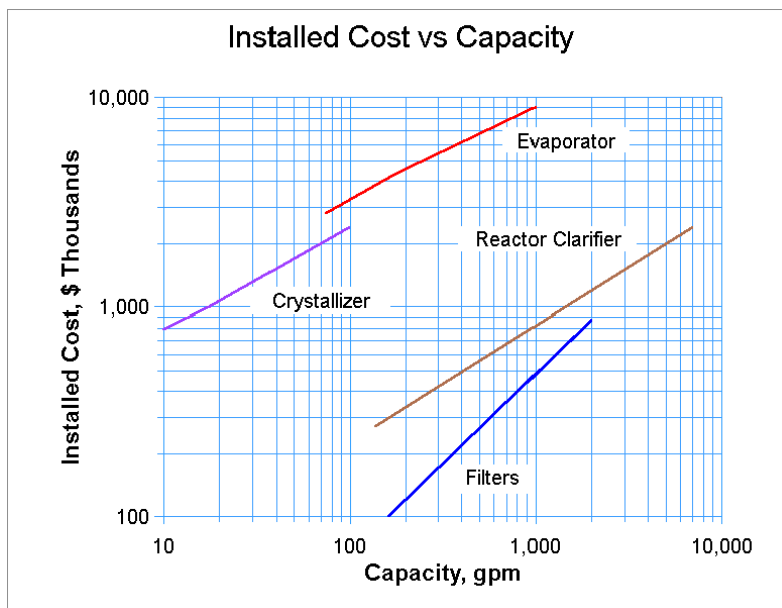


Figure 5-13
Installed Cost vs Capacity

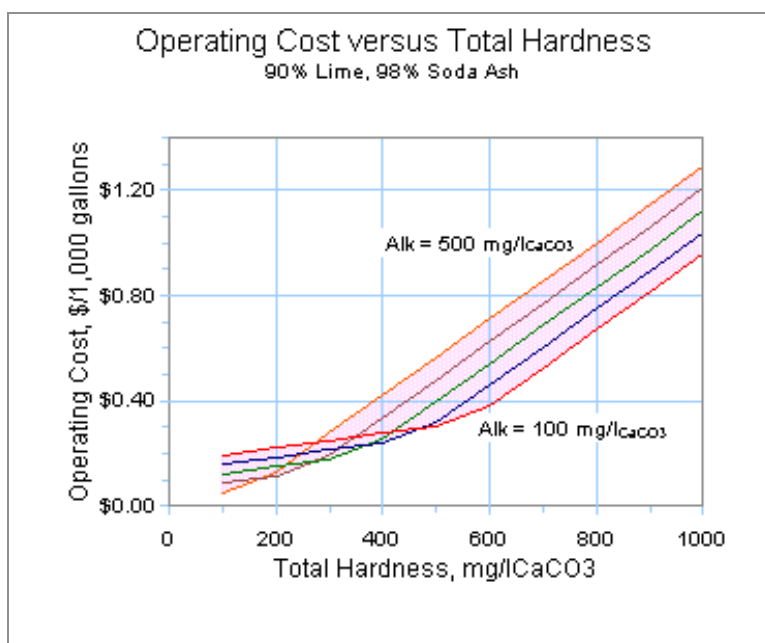


Figure 5-14
Operating Cost vs Total Hardness

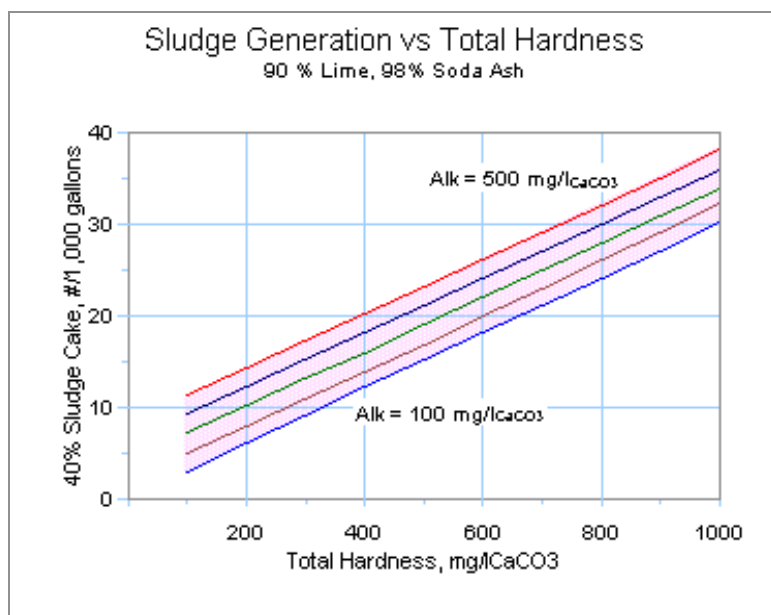


Figure 5-15
Sludge Generation vs Total Hardness

6

EMERGING TECHNOLOGIES

6.1 Introduction

Emerging treatment technologies and processes that may make it possible to use degraded and reclaimed water are identified. An effort was made to identify processes not considered in the mainstream of treatment approaches. The technologies in this section focus primarily on environmental contaminants typically associated with degraded water - heavy metals, pesticides and organic compounds. One technology involves de-ionization (salinity reduction). Many of the technologies are in the early phases of research and development and some are commercial. Contact information is provided for each technology.

6.2 Heavy Metals

There is a significant amount of research being developed in this area. Four technologies are discussed - two commercial and two developmental.

Chrome (+6) Removal via Anion Liquid Ion Exchange

A common approach to chrome (+6) removal involves reduction to chrome (+3) and co-precipitation by ferric salts. The process generates a significant amount of sludge which usually requires special handling and disposal. The anion liquid exchange process (A-LIX) utilizes an immiscible amine that is mixed with the degraded water to be treated. A closed loop reactor circulates the ion-exchange amine where chrome (+6) is exchanged onto functionalized resin sites. After exchange, the water is separated from the amine and discharged. As resin capacity is reached, the process is paused for regeneration and the chromate is removed from the amine. To date, testing has yielded effluent chrome (+6) within discharge limits. This process is close to commercialization. The Department of Defense (via Tyndall Air Force Base) is planning a full scale test at Warner-Robbins Air Force Base and Watervliet Army Depot.

Lt. G. Graziano
Tyndall AFB, Florida
850-283-6064

Arsenic Removal via Selective Media

Like chrome, arsenic removal via ferric salt co-precipitation is also a common approach. A commercial process - selective electrochemically regenerated ion extraction (SERIX-A) has been developed for arsenic removal. The process utilizes an organic media with ligands which are highly selective towards arsenate and arsenite. The arsenic loading capacity of the media exceeds 2 percent by weight (of the media). Arsenic can reportedly be removed to levels of <1 µg/l. The media can be modified to remove chrome (+6) as well. The media is electrochemically regenerated with a fixed volume of eluant. Depending on the application, metals can also be recovered (e.g. metal plating rinse water).

Electrochemical Design Associates, Inc.
Berkeley, California
510-704-2940

Imprinted Sorbent Materials for Heavy Metals Removal

This technology utilizes the attracting force of highly charged iron oxide to dissolved metals without generating sludge. An imprinted sorbent consists of colloid-like hydrated iron (ferrihydrite particles) dispersed into an organic polymer matrix such as an ion-exchange resin or fused into a granular inorganic base material. During the imprinting process, the ferrihydrite binding sites and the attracted metal ions (zinc (+2) and arsenic (+5)) develop a permanent (imprinted) stereo-specific relationship, i.e. specific to the shape and size of an ion. Consequently, the imprinted sorbent can very selectively capture target metal ions over a wide range of pH in the presence of other competing ions. A simple regeneration process can be utilized to regenerate the sorbent. The process is in the early development stage.

A. K. SenGupta
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Bethlehem, Pennsylvania
610-758-3534

Bioadsorbents for Heavy Metal Removal

This technology, which is in the research phase, utilizes genetically engineered e-coli bacteria to develop cell-surface metal sequestration capability. This mechanism differs from cellular uptake where metals are metabolized within the cell. E-coli bacteria are infused into a cellulose support media (e.g. non-functionalized ion exchange resin) and are loaded into typical test columns. The bacteria is genetically “engineered” to develop sequestant binding sites on the cell surface which enables it to bind heavy metals such as cadmium, mercury and lead. Sequestering sites are being developed with high affinities for specific metals. Support media and regeneration procedures are being evaluated. The process is in the early development stage.

W. Chen
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Riverside, California
909-787-2982

6.3 Pesticides

Two pesticide decomposition technologies are presented - a passive treatment approach and biological treatment.

Zeolite Technique Speeds Pesticide Decomposition

A research team at the university of Maine is in the early phases of evaluating a passive process (non-equipment treatment approach) that decomposes pesticides. When pesticide-containing water is exposed to A-type zeolite and sunlight, pesticides rapidly decompose, e.g. the decomposition rate for malathion, carbofuran and carbaryl were 35, 120 and 164 times faster, respectively. Zeolite is a natural mineral with an ordered, open/porous structure. A pesticide molecule partially enters a channel in the zeolite matrix where it is held in place. Natural sunlight (or light of a specific frequency) affects the chemical bond that hold the nitric oxide constituent of the molecule and releases oxygen and nitrogen gas. This technology has the potential of treating water without generating a liquid or solid waste stream. The research is in the early development stage.

H. H. Patterson
University of Maine
Orono, Maine
207-581-1178

Detoxification of Organophosphorous Pesticides

This technology utilizes a natural enzyme (phosphotriesterase) to degrade organophosphate pesticides such as parathion. A biological process will be used to direct the enzyme onto the surface of easily-reproduced e-coli bacteria (e-coli does not manufacture this enzyme). Initially, enzyme/surface stability, cell growth and degradation kinetics will be monitored under various operating conditions. Enzyme expression hosts (bacteria that manufacture the enzyme) and support media will be optimized. Also, optical biosensors will be developed to measure the decomposition of organophosphates. This technology also has the potential of treating water without generating a liquid or solid waste stream. The process is in the early development stage.

A. Mulchandani
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Riverside, California
909-787-6419

6.4 Organic Compounds

Three technologies are presented - two in the early stage of development and one that is recently commercial.

Modified PMDS Membranes to Remove Polar Organic Compounds

This technology, which is in the early stage of development, involves adding functionalized amine groups to PMDS (polydimethylsiloxane), a common dense-phase membrane. The amine groups are added directly to the polymer backbone, and as such, crosslink the polymer strands. In this manner, the permeability (and thus opportunity for removal) of polar organic compounds is increased five fold by incorporating polar functionality (the control compound is phenol at this stage of the research). This effort is being conducted in parallel to bioreactor research utilizing PMDS as a support media for bacteria. Therefore, the increased permeability allows the bacteria to have more access to organic compounds to be decomposed. The degree of optimal functionalization and permeability is currently being evaluated.

F. K. Thompson
Imperial College of Science, Technology & Medicine
London, U.K.
44-1233-812401

Biofilter Removal of VOCs from Airborne Emissions

This technology is in its commercialization stage, but depending on the application, still requires some research. The primary advantage of this technology is VOC removal without combustion or GAC loading (and eventual offsite post treatment). The Air Resources Board of California funded this research to determine optimal operating conditions for biofilters to treat airstreams contaminated with volatile organic compounds (VOCs). The work relates to low concentration airstreams originating from groundwater treatment systems (treating degraded water), municipal effluent treatment plants and landfills. Optimal operating conditions and removal efficiencies were determined for a laboratory scale biofilter using continuous flow conditions. Process configuration were also varied, e.g. biofilter area versus depth. Experiments were conducted using varying gas flux, VOC loading and transient VOC loading. Excellent removal capabilities were observed, e.g. 99+ percent removal of toluene and hexane, 98 percent removal of dichloromethane, etc. However, there were mixed results for trichloroethylene.

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Adsorption of Organic Compound Using Hypercrosslinked Polymers

Hypercrosslinked polymer matrices (similar to macroreticular ion resin, i.e. an open pore structure) have unique properties in that they mimic the attributes of conventional adsorbents in gaseous and liquid phase processes, e.g. granular activated carbon. Hypercrosslinking is accomplished by heavily interconnecting a polymer backbone to itself and neighboring polymer strands. This creates a porous and rigid structure resembling GAC. Because of their porosity, these polymers attract and capture organic molecules including pesticides. Research is currently being conducted to determine sorption kinetics and equilibrium. Scale-up studies are also underway for a mobile test apparatus. Lastly, some commercial ion exchange resins could be modified (in the manufacturing process) to exhibit these properties allowing this technology to be easily produced with existing manufacturing methods.

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44-1509-222506

6.5 Deionization via Aerogels

Carbon aerogels are extremely light solids - void volume can reach 99.8 percent. Also, because of their highly interconnected structure they are rigid and have a high internal surface area. Carbon aerogel can be manufactured as film or sheet-like structures which are electrically conductive. A 2,000 gallon-per-day demonstration system has been operating to deionize water via capacitive deionization (CDI) using carbon aerogel sheets. CDI is an innovative process for removing charged ions (inorganic salts) from water. Opposite charges are placed on opposing carbon aerogel sheets to form an electrolytic cell. Cations (positively charged ions) are attracted to the negatively charged sheet and anions are attracted to the positively charged sheet. Ions are released after the aerogel sheets become "loaded", i.e. the charge on each sheet is reversed and the system is flushed. CDI using silica-based aerogels are already commercial and are used to remove trace levels of inorganic salts from water. However, because of the very high porosity of carbon aerogels, they promise to be much more efficient. Also, there are applications in perchlorate removal as well (some testing has been conducted). The process is in the early development stage.

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A

BIBLIOGRAPHY

Some of the references are annotated to assist the reader in understanding their content, limitations and value. Additional references, which were not cited in the report, are found in section A.2 of the bibliography and are offered as supplemental technical resources.

A.1 Referenced Citations

A.1.1 Referenced Citations - Chapters 1 and 2

1. Municipal Wastewater Reclamation Survey, California State Water Resources Control Board, May 2000

The survey summarizes water reclamation projects (using treated municipal effluent) in California. Projects are identified by treatment plant, treatment processes, wholesale and retail users, types of use (e.g. irrigation, industrial cooling, boiler feedwater, etc.) and annual use. The report is not complete (information is gathered informally, also there is no data for five counties), but represents the types and amounts of reclaimed water used in California today.

2. California Water Plan Update, Bulletin 160-98, Department of Water Resources, November 1998

This report is issued every five years by the State of California (mandated by the California Water Code). It is an analysis of past and projected water needs of agriculture, urban and environmental (maintenance of habitat) needs, water quality, state and federal regulatory issues, major water management issues and projects, etc. Past and future water use is analyzed in detail in the major use categories using drought and non-drought scenarios. Water reclamation using municipal effluent is briefly discussed.

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This is a very early paper involving cooling tower water quality parameters. The paper suggests operating limits for a number of scaling species as well as rules of thumb to calculate pH. Water quality requirements from this paper are cited in Table 2-1 of the report.

5. EPRI CS-2276, Design and Operating Guidelines Manual for Cooling-Water Treatment, Section 5, March 1982

Comprehensive guidelines developed to evaluate all aspects of cooling water treatment: design guidelines, process model documentation and user's manual, equilibrium model documentation and user's manual and handbook of generalized operational guidelines.

6. EPRI WO9071, Cooling Water Treatment Manual (unpublished), September 22, 1998

This document broadly covers water-related issues for cooling towers, e.g. chemistry (relating to scaling, corrosion and bio-fouling), treatment, monitoring and maintenance concerns. Case studies are also evaluated based on source water chemistry and cooling tower design. For some parameters, water quality criteria is presented in gradations from conservative rules of thumb to predictive analysis using specific software. The reader is referred to EPRI software that can be used for the prediction of chemical scaling in cooling towers.

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Although the focus of this paper is water reuse, it provides cooling tower water quality control parameters for a wide variety of chemical constituents typically found in petroleum refinery. It should be noted that refinery cooling water is challenging and control limits for typical scaling constituents are higher than those for power plant cooling applications. Pre-treatment technology for constituents of concern is also discussed. Water quality requirements from this paper are cited in Table 2-1 of the report.

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9. EPRI CS-5495, Microbial Corrosion in Fossil-Fired Plants, A Study of Microbiologically Influenced Corrosion and a Practical Guide for Its Treatment and Prevention, November 1987

This paper evaluated the extent and effects of microbiologically influenced (or induced) corrosion (MIC) in fossil-fired power plants. Fifty randomly selected power plants were surveyed. Techniques were developed to detect, treat and prevent MIC.

10. EPRI AP-109966, WinSEQUIL Version 2.0 (software), February 1999

WinSEQUIL is a software program developed by EPRI that calculates equilibrium chemistry and predicts the mineral scaling tendency of process water based on its chemical composition, pH and temperature. (A final version of the software has not been issued.)

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12. NPDES—National Pollutant Discharge Elimination System (from Clean Water Act, 33U.S.C.1251 *et seq.*)
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This paper evaluates a patented (not yet commercialized) soap-based compound (carboxylic acid-amine) to operate cooling towers with high-hardness feed water at 10-12 cycles of concentration. Optimal doses at a pH of 8.7 effectively controlled mineral deposition.

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This paper broadly discusses cooling (and other) systems with respect to treatment processes, chemical treatment, monitoring and automated control. The paper focuses more on industry trends than specific operating information.

5. Richardson, J., Reinsalu, M., A. and Heinz, K., D., "A New On-Line Monitoring and Control Capability for Cooling Water Programs", *CTI Journal*, Vol. 15, No. 1, Winter, 1994, pp. 58-71

A monitoring and control process which measures active treatment components is discussed. The instrument incorporates both measurement and control for scaling and corrosion chemicals. The monitor is also capable of discerning/filtering analytical interference. On-line Molybdate (corrosion inhibition for mild steel) and tolytriazole (corrosion inhibition for copper alloys) protocols were field tested.

6. Trulear, M., G. and Richardson, J., "Actives-Based Monitoring and Control for Improved Cooling System Management and Performance", *CTI Journal*, Vol. 21, No. 1, Winter, 2000, pp. 10-21

This paper addresses an evaluation of on-line measurement of treatment-program actives, e.g. dispersant polymer, phosphonate, phosphate and molybdate. On-line measurement ensures

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This paper discusses a side-stream treatment cooling tower application using high-silica feedwater for a zero-discharge power plant. Feedwater variability and operating problems are discussed. System upgrade issues are also discussed, e.g. materials of construction, chemistry control, monitoring, etc.

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Corrosion

10. Sullivan, P. J., "A Mechanistic Study of Corrosion Inhibition by Phosphonates", CTI Journal, Vol. 16, No. 1, Winter, 1995, pp. 62-72

This paper evaluates the interaction of all-organic scale inhibition and oxidizing biocides. High hardness water poses a scaling problem and the use of organo-phosphonates such as HPA, PBTC and HEDP have been successful in controlling scale. Oxidizing biocides compromise control by reacting with phosphonates and creating ortho-phosphates which readily react with calcium to form scale. An amine/HPA blend was evaluated to reduce the impact of oxidizing biocides on phosphonate decomposition.

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This study investigates the inhibition of copper/iron galvanic corrosion using molybdate and nitrite together or separately. The study shows that a threshold pH (>6) is required for inhibition. Synergistic iron surface reactions with nitrite and molybdate are also explored. Nitrate can be an excellent corrosion inhibitor for mild steel.

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Triazole copper corrosion inhibitors are discussed. This family of inhibitors is used extensively today for the protection of copper-bearing metals typically found in power plant heat condensers, e.g. 90-10 copper nickel, admiralty, etc. The paper examines the correlation between the structure of aromatic triazoles and the ease of their biodegradability.

Scale

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This paper evaluates the synergism of a blend of PAPEMP (phosphonate scale inhibitor), hydroxyphospho carboxylic acid (steel corrosion inhibitor) and a sulfonated polymer (scale dispersant). Pilot (portable cooling tower) and case studies operating at very high pH (8.5 - 9.0) with no acid addition for alkalinity control. Scale control as well as corrosion inhibition were attained using certain combinations of the inhibitors and dispersant.

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This article generally describes water treatment issues involving scaling, corrosion and biological control. Commercially available chemical treatment programs are broadly discussed. The article was designed for plant staff (without a chemical background) that are responsible for cooling tower treatment.

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This paper details the experience of operating without a blowdown stream on a very small cooling system. The system could not discharge to the sewer because of regulatory restrictions. Several modes of operation were tried - with and without pH control, using commercial products operating at alkaline pH and using products that were specifically designed for high TDS and alkaline pH.

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This paper summarizes a series of jar tests that evaluated the use of a bio-dispersant to enhance biocide effectiveness. The bio-dispersant effectively removed biological film from surfaces. Also, the bio-dispersant increased biocide efficacy.

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This paper outlines studies conducted with halogen-resistant calcium carbonate scale inhibitor and copper alloy corrosion inhibitor. Halogens used for biological control can degrade typically used inhibitors. A non-phosphonate calcium carbonate inhibitor and a modified azole copper inhibitor were evaluated. Field studies showed successful results and reduced costs.

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This article is a transcript of a panel discussion on the state-of-the-practice of ozone treatment of cooling water. The discussion covers a broad range: water chemistry, oxidizing reactions, condenser and tower film fouling, ozone generator and injector design, etc.

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This paper discusses a highly-accurate automated chlorination feed and control system. The system utilizes a sensitive ORP probe (oxidation-reduction potential) probe to control residual chlorine to ± 0.1 mg/l.

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23. Ferguson, R. J., "Computerized Ion Association Model Profiles Complete Range of Cooling System Parameters", *International Water Conference*, October 1991

This paper discusses mathematical approaches used to predict the scaling tendencies of water containing a variety of ions. Equilibrium relationships and known ion associations are used to predict the behavior of scaling species. Note, this approach has been developed fully and a variety of modeling software packages are available today.

24. Ferguson, R. J., "Developing Scale Inhibitor Dosage Models", *Water Tech '92*, 1992

This paper takes the developmental work of equilibrium relationships and ion association used to produce scaling software and predicts scaling behavior using commercially available inhibitors. Note, there is a variety of modeling software packages are available today.

B

FORMULAS AND CALCULATION PROCEDURES

B.1 Langelier and Ryznar Indices

As stated previously, the Langelier Saturation Index and Ryznar Stability Index were originally developed to identify scaling (calcium carbonate) and corrosion tendencies of water in supply piping. These indices, which are still in wide use today, are considered very conservative. Most scaling and corrosion conditions identified by these indices can typically be controlled by specialty chemicals. Their usefulness is therefore limited, but because of their common use, the following calculation procedure is provided in Table B-1. The Puckorius Scaling Index modifies the Ryznar Stability Index by calculating the pH of the bulk water, and thus, more accurately predicts scaling conditions.

B.2 Formulas - Maximum Allowable Cycles of Concentration

A series of formulas are provided in Table B-2 for calculating the maximum allowable cycles of concentration for six cooling tower water criteria. A procedure for calculating the limiting cycles of concentration is provided on the second page of Table B-2.

Refer to Table B-3 for concentration conversion factors. Source water data often provides concentrations for key constituents as mg/l as the ion, e.g. mg/l as Ca, or in the case of phosphate as mg/l as phosphorous. The factors can be utilized to convert source water concentrations to the equivalents required by the formulas in Table B-2.

Table B-1
Langelier, Ryznar and Puckorius Indices - Simplified Calculation

Ca		Alkalinity		TDS		Temp	
mg/l CaCO ₃	pCa	mg/l CaCO ₃	pAlk	mg/l	C _{TDS}	°F	C _{Temp}
50	3.30	50	3.01	500	2.16	80	-0.00
100	3.01	100	2.71	1,000	2.19	90	-0.11
200	2.72	150	2.54	1,500	2.20	100	-0.21
300	2.55	200	2.41	2,000	2.21	110	-0.31
400	2.43	250	2.32	2,500	2.22	120	-0.41
500	2.34	300	2.24	5,000	2.24	130	-0.49
600	2.26	350	2.17	7,500	2.24	140	-0.58
700	2.20	400	2.11	10,000	2.25	150	-0.66
800	2.14	450	2.06	15,000	2.26	160	-0.74
900	2.09	500	2.02	20,000	2.26		
1,000	2.05			30,000	2.26		

$$pH_s = pCa + pAlk + C_{TDS} + C_{Temp}$$

$$\text{Langelier Saturation Index, LSI} = pH_{\text{Actual}} - pH_s$$

$$\text{Ryznar Stability Index, RSI} = 2 \times pH_s - pH_{\text{Actual}}$$

$$\text{Puckorius Scaling Index, PSI} = 2 \times pH_{\text{eq}} - pH_s$$

$$pH_{\text{eq}} = 1.465 \times \log[\text{Total Alkalinity}] + 4.54$$

Detailed Calculation Procedure.....

$$pCa = 4.932 - 0.9618 \log(Ca)$$

$$pAlk = 4.683 - 0.9870 \log(Alk)$$

$$C_{TDS} = 2.306 - 1.527 \times 10^{-7} TDS - 1.190 TDS^{-1/3}$$

$$C_{Temp} = 2.358 \times 10^{-5} Temp^2 - 0.0149 Temp + 1.037$$

$$[\text{Total Alkalinity}] = [H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}]$$

Ca as mg/l CaCO₃

Alkalinity as mg/l CaCO₃

TDS as mg/l

Temp as °F

Total Alkalinity as mg/l CaCO₃

Table B-2
Formulas - Maximum Allowable Cycles of Concentration

(1) Ca (in absence of PO₄)

$$N_{Ca} = 900/Ca_{Feed}$$

Where:

$$Ca_{Feed} = \text{Ca in cooling tower feed water, mg/l}_{CaCO_3}$$

(2) CaSO₄

$$N_{CaSO_4} = \{Alk_{CT} + [Alk_{CT}^2 + 4Ca_{Feed}(SO_4_{Feed} + Alk_{Feed})K_{CaSO_4}]^{0.5}\} / [2Ca_{Feed}(SO_4_{Feed} + Alk_{Feed})]$$

Where:

$$Alk_{CT} = \text{cooling tower alkalinity, mg/l}_{CaCO_3}$$

$$Ca_{Feed} = \text{Ca in cooling tower feed water, mg/l}_{CaCO_3}$$

$$SO_4_{Feed} = \text{SO}_4 \text{ in cooling tower feed water, mg/l}_{CaCO_3}$$

$$Alk_{Feed} = \text{alkalinity in cooling tower feed water, mg/l}_{CaCO_3}$$

$$K_{CaSO_4} = 1.300 \times 10^6 \text{ mg/l}_{CaCO_3}^2$$

(3) Mg x SiO₂

$$N_{MgSiO_2} = (75,000/Mg_{Feed}/SiO_{2Feed})^{0.5}$$

Where:

$$Mg_{Feed} = \text{Mg in cooling tower feed water, mg/l}_{CaCO_3}$$

$$SiO_{2Feed} = \text{SiO}_2 \text{ in cooling tower feed water, mg/l}_{SiO_2}$$

(4) SiO₂

$$N_{SiO_2} = 150/SiO_{2Feed}$$

Where:

$$SiO_{2Feed} = \text{SiO}_2 \text{ in cooling tower feed water, mg/l}_{SiO_2}$$

(5) TDS

$$N_{TDS} = 70,000/TDS_{Feed}$$

Where:

$$TDS_{Feed} = \text{TDS in cooling tower feed water, mg/l}$$

(6) Cooling Tower pH

$$pH = 1.465 \log(Alk_{CT}) + 4.5$$

Where:

$$Alk_{CT} = \text{cooling tower alkalinity, mg/l}_{CaCO_3}$$

(7) Ca₃(PO₄)₂ (Note 2)

$$N_{Ca_3(PO_4)_2} = (K_{spCa_3(PO_4)_2} / Ca_{Feed}^3 / PO_4_{Feed}^2)^{0.2}$$

Where:

$$\log(K_{spCa_3(PO_4)_2}) = [f_1(TDSc_T) \times pH + f_2(TDSc_T)] \times (1.143 - 2.107 \times 10^{-3}T)$$

$$f_1(TDSc_T) = -2.920 \times 10^{-6}TDSc_T + 8.078 \times 10^{-3}TDSc_T^{1.4} - 3.018$$

$$f_2(TDSc_T) = 1.143 \times 10^{-4}TDSc_T - 3.004 \times 10^{-2}TDSc_T^{1.4} + 29.034$$

$$T = \text{Cooling water return temperature, } ^\circ\text{F}$$

$$7.0 < pH < 7.5$$

$$TDSc_T = \text{cooling tower TDS, mg/l}$$

$$500 \text{ mg/l} < TDSc_T < 20,000 \text{ mg/l}$$

$$Ca_{Feed} = \text{Ca in cooling tower feed water, mg/l}_{CaCO_3}$$

$$PO_4_{Feed} = \text{PO}_4 \text{ in cooling tower feed water, mg/l}_{PO_4}$$

Table B-2 Continued on next page.....

Table B-2 (continued)

1. Calculate maximum N_{Max} (cycles of concentration) in the order shown for equation sets (1) thru (5).
2. Calculate TDS based on smallest value of N_{Max} determined in Step 1 above.
3. Assume pH = 7.0.
4. Calculate $N_{Ca_3(PO_4)_2}$ - equation set (7).
5. Note, if $N_{Ca_3(PO_4)_2} < 1$, water is already saturated with $Ca_3(PO_4)_2$ and *cannot be used for cooling with out pretreatment*.
6. If $N_{Ca_3(PO_4)_2} < N_{Max}$, $N_{Max} = N_{Ca_3(PO_4)_2}$.
7. If $N_{Ca_3(PO_4)_2} > N_{Max}$, N_{Max} is the limiting concentration parameter.
8. If $N_{Ca_3(PO_4)_2} > N_{Max}$, pH can be increased incrementally by 0.1 units (repeat Steps 3 and 4) until $N_{Ca_3(PO_4)_2} = N_{Max}$.
9. Do not exceed pH = 7.5 when seeking N_{Max} since $Ca_3(PO_4)_2$ is difficult to control. *Corrosion is easier to control at higher pH.*
10. Refer to Table B-3 for conversion factors.

**Table B-3
Concentration Conversion Factors**

Ca, mg/l x 2.50	Ca, mg/l _{CaCO3}
Mg, mg/l x 4.12	Mg, mg/l _{CaCO3}
CO ₂ , mg/l x 0.88	CO ₂ , mg/l _{CaCO3}
H ₂ CO ₃ , mg/l x 1.24	H ₂ CO ₃ , mg/l _{CaCO3}
HCO ₃ , mg/l x 1.22	HCO ₃ , mg/l _{CaCO3}
CO ₃ , mg/l x 0.60	CO ₃ , mg/l _{CaCO3}
SO ₄ , mg/l x 1.04	SO ₄ , mg/l _{CaCO3}
PO ₄ , mg/l _P x 3.07	PO ₄ , mg/l _{P04}

C

PERFORMANCE INDICATORS FOR REACTOR CLARIFIERS (SOFTENERS)

This appendix contains sections of the US Filter Water and Wastewater Treatment Data Book, Sections 51 to 59. This information can be used to predict the following performance indicators for make-up and side-stream reactor clarifiers:

- Effluent chemistry - calcium, magnesium and alkalinity
- Chemical consumption - lime and soda ash.

Refer to Figure 5-11 and Figure 5-12 to predict silica reduction for make-up softening (60 to 80°F) and side-stream softening (104°F), respectively.

SECTION 51.

COLD LIME (OR LIME SODA) WATER SOFTENING PROCESSES AS CARRIED OUT IN THE PERMUTIT PRECIPITATOR

The following material on the cold lime, or lime soda, water softening processes as carried out in the Permutit Precipitator has not been previously published, except in fragmentary form. This complete data enables engineers to become readily acquainted with the compositions of the effluents that may be produced from any water supply by various treatments; the amounts of chemicals required for processing; and to select the most economical and adaptable method for each problem. This data does not apply to the older types of cold lime, or lime soda, water softening equipment in which completed reactions are not obtained.

The Economics of Treatment

When calcium hardness is to be removed; it is precipitated as calcium carbonate (CaCO_3).

When magnesium hardness is to be removed, it is precipitated as magnesium hydroxide ($\text{Mg}(\text{OH})_2$).

Each unit of calcium bicarbonate hardness (calcium alkalinity) removed requires *one* equivalent of lime.

Each unit of magnesium bicarbonate hardness (magnesium alkalinity) removed requires *two* equivalents of lime.

Each unit of calcium noncarbonate hardness removed requires *one* equivalent of soda ash.

Each unit of magnesium noncarbonate hardness removed requires *one* equivalent of soda ash *plus one* equivalent of lime.

NOTE: For the chemical reactions involved see Section 60.

Since more chemicals are required it is more costly to remove magnesium hardness than calcium hardness. This is shown in the following figures which are based on removing 100 ppm of hardness from 1,000,000 gallons of water. The cost figures of the chemicals employed vary in different localities.....

Comparative Costs for Removing 100 ppm of Hardness from 1,000,000 Gallons of Water

	Cost
Calcium bicarbonate hardness (expressed as CaCO_3) - 520 lb. lime	(local pricing)
Magnesium bicarbonate hardness (expressed as CaCO_3) - 1040 lb. lime	(local pricing)
Calcium noncarbonate hardness (expressed as CaCO_3) - 90 lb. soda ash	(local pricing)
Magnesium noncarbonate hardness (expressed as CaCO_3) - 900 lb. soda ash + 520 lb. lime	(local pricing)

Therefore, the removal of calcium bicarbonate hardness is the cheapest. Compared with it, the cost of removal of the other forms of hardness are (approximately):

Magnesium bicarbonate hardness..... Twice as much

Calcium noncarbonate hardness..... Five times as much

Magnesium noncarbonate hardness..... Six times as much

For many purposes, so called "complete treatment" is both unnecessary and uneconomical. This applies, for instance, to municipal water softening where the problem is simply to reduce the total hardness to a given figure (usually about 85 ppm); to the treatment of cooling waters where only the calcium bicarbonate hardness may be the scale forming factor; to the treatment of certain paper mill waters where calcium bicarbonate hardness is the troublesome factor; to the treatment of waters for beverage manufacture where alkalinity reduction is the prime requisite.

In other cases, removal of other hardness constituents to various degrees may be required. In the Permutit Precipitator, such variations in treatment may be readily and speedily carried out with the production of what- ever character of effluent is required for any specific purpose. Since the dosage of chemicals depends on the amounts and kinds of hardness to be removed, it is first shown how to predict the treated water analysis and second how to calculate the chemical dosage required. The following methods of calculation are arranged in the order of economy of treatment.

- | | |
|--|---|
| 52. Solubilities of Calcium Carbonate-pH Values | 57. Reduction of Alkalinity and Noncarbonate Hardness |
| 53. Solubilities of Magnesium Hydroxide-pH Values | 58. Railway Lime Soda Treatment-"Excess Chemical Treatment" |
| 54. Dosages and Effects of Coagulants-Modified Water Analysis-Definitions of Terms | 59. Reduction of Alkalinity in Waters Containing Sodium Alkalinity |
| 55. Reduction of Calcium Alkalinity by the Cold Lime Process | 60. Chemical Reactions in Cold Lime, Lime Soda and Chloride Process |
| 56. Reduction of Calcium and Magnesium Alkalinities by the Cold Lime Process | |

SECTION 52.

SOLUBILITIES OF CALCIUM CARBONATE - pH VALUES

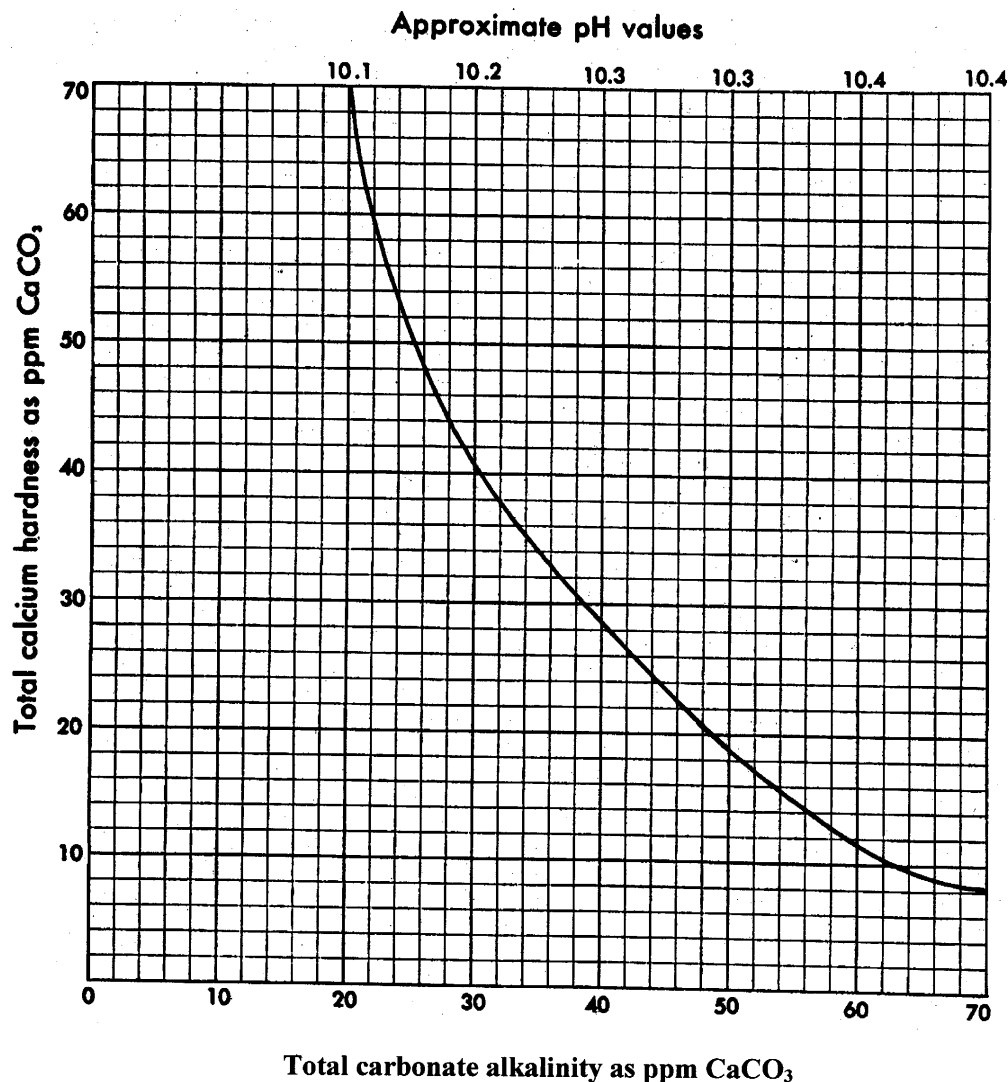
The cold lime (or lime soda) process is capable of yielding a variety of effluents, depending on the composition of the raw water and on the dosages of chemicals added. The dosages of chemicals required to effect these various results are based on the following principles:

Removal of Free Carbon Dioxide: Lime removes free carbon dioxide forming calcium carbonate.

Removal of Calcium: Lime reacts with calcium alkalinity forming calcium carbonate. Soda ash reacts with calcium noncarbonate hardness forming calcium carbonate. The solubility of calcium carbonate is affected by the presence of the common ions of calcium (Ca^{++}) or carbonate (CO_3^{--}) as shown in the following curve:

Calcium Hardness Reduction with the Permutit Precipitator

Guaranteed results



NOTE: It will be noted, from the, above, curve, that calcium hardness can not be, depressed below approximately 35 ppm without having another carbonate (sodium carbonate or magnesium carbonate) present. For the sake of simplicity in calculating the compositions of effluents in the following pages, with the exception of Railway Lime Soda Treatment, the solubility of calcium carbonate has been taken as being 35 ppm. If other calcium ions or carbonate ions are present, their effect on the composition of the effluent may be obtained from the above curve.

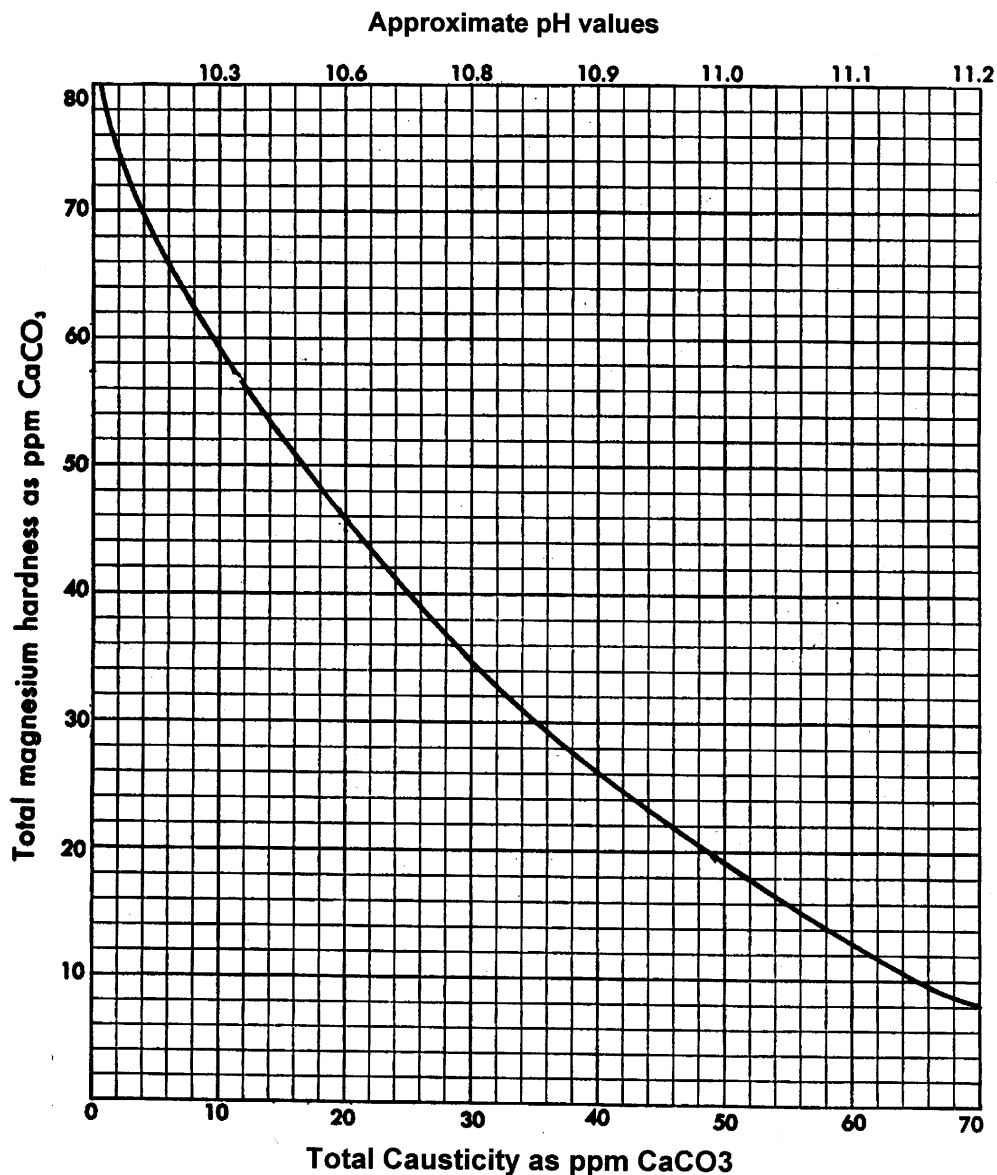
SECTION 53.

SOLUBILITIES OF MAGNESIUM HYDROXIDE - pH VALUES

Removal of Magnesium: When calcium is precipitated as calcium carbonate, some magnesium is carried down with it as magnesium hydroxide. For purposes of calculation, this may be assumed to average about 10% of the magnesium hardness present. For further reduction of magnesium hardness, additional dosages of lime (or lime and soda ash) are required. The solubility of magnesium hydroxide is affected by the presence of the common ions of magnesium (Mg^{++}), or hydroxyl (OH^-) (causticity) as shown in the following curve:

Magnesium Hardness Reduction with the Permutit Precipitator

Guaranteed results



NOTE: It will be noted, from the above curve, that magnesium hardness can not be depressed below about 80 ppm without having causticity (hydroxyl ions) present. From 80 ppm down to approximately 33 ppm of magnesium hardness, this causticity is due to magnesium hydroxide. In order to depress the magnesium hardness further, another hydroxide (sodium hydroxide or calcium hydroxide) must be present. In all calculations involving magnesium hardness reduction in the following pages, the above curve should be used to obtain the amounts of residual magnesium hardness in the effluents.

SECTION 54.

**DOSAGES AND EFFECTS OF COAGULANTS:
MODIFIED WATER ANALYSIS DEFINITION OF TERMS**

Dosages and Effects of Coagulants: A coagulant is usually employed in the cold lime (or lime soda) process of water softening. The coagulant may be aluminum sulfate (filter alum), ferrous sulfate (copperas), ferric sulfate or sodium aluminate. The coagulant aids in settling the precipitates formed in the process. It also affects the alkalinity and free carbon dioxide content of the raw water analysis. The effect on the total sulfate content is also given. Dosage examples are as follows:

Modified Water Analysis: *The Modified Water Analysis is used as the basis of all calculations.* The modified water analysis is obtained by making the following changes (depending on the coagulant used) in the alkalinity and free carbon dioxide content of the raw water analysis. The effect on the total sulfate content is also given. Dosage examples are as follows:

		MODIFIED ANALYSIS								
		Using 20 ppm Aluminum Sulfate		Using 20 ppm Ferrous Sulfate		Using 10 ppm Ferric Sulfate		Using 10 ppm Sodium Aluminate		
Alkalinity expressed as CaCO ₃	Raw Water Analysis	No. of ppm	Subtract	9 ppm	Subtract	8 ppm	Subtract	6 ppm	Subtract	6 ppm
Free CO ₂ expressed as CaCO ₃	No. of ppm	Add	8 ppm	Add	7 ppm	Add	8 ppm	Add	8 ppm	6 ppm
Sulfate expressed as CaCO ₃	No. of ppm	Add	9 ppm	Add	8 ppm	Add	6 ppm	None		

The term "Original" as used in the text refers to the figures in the modified analysis.
For exact dosage determinations, see page 36.

Definition of Terms: By inspection of the modified water analysis, the presence or absence of the following constituents and the amounts of those present may be determined as follows:

Calcium alkalinity.....	= Calcium hardness or alkalinity, whichever is smaller (if equal either one)
Magnesium alkalinity.....	= Magnesium hardness, if alkalinity is equal to or greater than total hardness
Magnesium alkalinity.....	= Alkalinity - calcium hardness, if alkalinity is less than total hardness
Sodium alkalinity.....	= Alkalinity - total hardness
Calcium noncarbonate hardness.....	= Calcium hardness - calcium alkalinity
Magnesium noncarbonate hardness...	= Magnesium hardness - magnesium alkalinity
Total noncarbonate hardness.....	= Total hardness - alkalinity

NOTE: In the above, if any computation yields a zero or negative result, none of that substance is present.

SECTION 55.

REDUCTION OF CALCIUM ALKALINITY BY THE COLD LIME PROCESS

Composition of Effluent: The treatment for calcium alkalinity reduction results in removing the free carbon dioxide, reducing the calcium alkalinity to 35 ppm and removing approximately 10% of the magnesium hardness (the magnesium hardness reduction is usually somewhat less than 10% if the magnesium hardness of the water is low, and slightly over 10% if it is high). The composition of the effluent will be as follows:

- | | | |
|--------|--------------------------|---|
| (1) | Free carbon dioxide..... | = None |
| * (2) | Calcium hardness..... | = (Original calcium hardness + 35 ppm)-original calcium alkalinity |
| (3) | Magnesium hardness..... | = 90% of original magnesium hardness |
| (4) | Total hardness..... | = The sum of (2) and (3) |
| ** (5) | Alkalinity..... | = (Original alkalinity + 35 ppm)-original calcium alkalinity 10% of original magnesium hardness |
- *Case 1: The equation, as given, holds true if the original magnesium alkalinity equals or exceeds 10% of the original magnesium hardness.
- Case 2: If no original magnesium alkalinity is present, 10% of the original magnesium hardness will be converted to calcium hardness, and this amount should be added to the result obtained in (2) before computing (4).
- Case 3: If original magnesium alkalinity is present but in an amount of less than 10% of the original magnesium hardness, then 10% of the original magnesium hardness - original magnesium alkalinity is the amount that will be changed to calcium hardness, and this amount should be added to the result obtained in (2) before computing (4).
- **Case 1: The equation, as given, holds true if the original magnesium alkalinity equals or exceeds 10% of the original magnesium hardness.
- Case 2: If no original magnesium alkalinity is present, omit the "10% of original magnesium hardness" from the equation.
- Case 3: If original magnesium alkalinity is present but in an amount of less than 10% of the original magnesium hardness, then the original magnesium alkalinity should be substituted in place of "10% of the original magnesium hardness" in the equation.

SECTION 55. (continued)

Check on Calculated Compositions of Effluent: There should be no change in the noncarbonate hardness or sodium alkalinity.

Alkalinity and pH of Effluent: The effluent will contain 35 ppm of carbonate alkalinity. Any alkalinity in excess of 35 ppm will be bicarbonate alkalinity. The pH of the effluent will be between 9.0 and 10.2.

Dosages of Lime Required: The dosages of commercial hydrated lime (93% Ca(OH)₂) or commercial chemical lime (90% CaO) required in pounds per 1000 U. S. gallons, will be as follows:

	93% Hydrated Lime	or	90% Chemical Lime
	-----Lbs. Per 1000 gal.-----		
Free carbon dioxide as ppm CO ₂	X .0151		X .0118
Calcium alkalinity as ppm CaCO ₃	X .00663		X .00519
Magnesium noncarbonate hardness removed as ppm CaCO ₃	X .00663		X .00519
Magnesium alkalinity removed as ppm CaCO ₃	X .01326		X .01038

SECTION 56. **REDUCTION OF CALCIUM AND MAGNESIUM ALKALINITES BY THE COLD LIME PROCESS**

Composition of Effluent: The treatment with lime for the reduction of both calcium alkalinity and magnesium alkalinity results in removing the free carbon dioxide; reducing the calcium hardness to 35 ppm; and reducing the magnesium hardness to a point consistent with the desired characteristics of the effluent and economy of treatment. This point; in single stage treatment, varies depending on the composition of the modified water analysis and the results desired.

For all cases, see the curve on magnesium hardness removal in section 53. When the point to which the magnesium hardness is to be reduced is determined, the composition of the effluent will be:

- (1) Free carbon dioxide..... = None
- (2) Calcium hardness..... = 35 ppm
- (3) Magnesium hardness..... = Any desired amount down to minimum*
- (4) Total hardness..... = The sum of (2) and (3)
- (5) Alkalinity..... = (Original alkalinity + 35ppm) - (Original calcium hardness + Magnesium hardness reduction)

* Minimum magnesium hardness that is economical may be determined as follows:

If sodium alkalinity is present in modified analysis in an amount equal to:

62 ppm or less

Total causticity for magnesium hardness - Final magnesium hardness = Sodium alkalinity

Greater than 62 ppm

Final magnesium hardness = 8ppm

If noncarbonate hardness is present in modified analysis in an amount:

Less than 80 ppm

Final magnesium hardness - total causticity for magnesium hardness = Noncarbonate hardness

80 ppm or more

Final magnesium hardness..... = Noncarbonate hardness

Check on Calculated Compositions of Effluent: There should be no change in the noncarbonate hardness or sodium alkalinity.

Alkalinity and pH of Effluent: If the treatment is carried out so that no causticity is left in the effluent, the alkalinity will be all carbonate alkalinity. If carried out so that causticity is present, the amount of causticity may be determined from section 53 and the remainder will be carbonate alkalinity. The pH of the effluent will be approximately 10.2 if no causticity is present. If causticity is present, the approximate pH may be determined from section 53.

Section 56. (Continued)

Dosages of Lime Required: The dosages of commercial hydrated lime (93% Ca(OH)_2) or commercial chemical lime (90% CaO) required, in pounds per 1000 U. S. gallons, is as follows:

	93% Hydrated Lime	or	90% Chemical Lime
	-----Lbs. Per 1000 gal.-----		
Free carbon dioxide as ppm CO_2	X .0151		X .0118
Alkalinity as ppm CaCO_3	X .00663		X .00519
Magnesium Alkalinity to be removed as ppm CaCO_3	X .00663		X .00519
Causticity in effluent as ppm CaCO_3	X .00663		X .00519

* If sodium alkalinity is present and if magnesium hardness is not to be reduced below 80 ppm, the dosage of lime may be reduced by an amount equivalent to one-half the sodium alkalinity present and the effluent will contain bicarbonate equivalent to one-half the sodium alkalinity.

SECTION 57. REDUCTION OF ALKALINITY AND NONCARBONATE HARDNESS BY THE COLD LIME SODA PROCESS

Classification: Waters containing noncarbonate hardness may be divided into three classes as follows:

Class 1 - contains

Free carbon dioxide
Calcium alkalinity
Calcium noncarbonate hardness
noncarbonate hardness

Class 2 - contains

Free carbon dioxide
Calcium alkalinity
Magnesium alkalinity
Magnesium noncarbonate hardness

Class 3 (acid waters) - contains

Free carbon dioxide
Calcium noncarbonate hardness
Magnesium noncarbonate hardness Magnesium

Class 1, Case 1: Composition of Effluent: Treatment for reduction of calcium alkalinity to 35 ppm and removal of part or all of the calcium noncarbonate hardness will result in an effluent of the following composition:

- (1) Free carbon dioxide..... = None
- (2) Calcium hardness..... = Whatever amount is desired down to 35 ppm
- (3) Magnesium hardness..... = 90% of original magnesium hardness
- (4) Total hardness..... = The sum of (2) and (3)
- (5) Alkalinity..... = 35 ppm

Check on Calculated Compositions of Effluent: The noncarbonate hardness should be reduced or the sodium alkalinity should be increased by the equivalent of the soda ash added (expressed as CaCO_3).

Alkalinity and pH of Effluent: The 35 ppm of alkalinity will be carbonate alkalinity. The pH will be approximately 10.2.

Dosages of Chemicals Required: The dosages of commercial hydrated lime (93% Ca(OH)_2) or commercial chemical lime (90% CaO) and commercial soda ash (98% Na_2CO_3) required, in pounds per 1000 U. S. gallons, will be as follows:

	93% Hydrated Lime	or	90% Chemical Lime	98% Soda Ash
	-----Lbs. Per 1000 gal.-----			
Free carbon dioxide as ppm CO_2	X .0151		X .0118	None
Calcium alkalinity as ppm CaCO_3	X .00663		X .00519	None
Magnesium noncarbonate hardness removed as ppm CaCO_3	X .00663		X .00519	X .00901
Magnesium alkalinity removed as ppm CaCO_3	None		None	X .00901

Class 1, Case 2: Composition of Effluent: Treatment for reduction of calcium hardness to 35 ppm and reduction of magnesium noncarbonate hardness to desired amount (see section 53) will result in an effluent having the following composition:

- (1) Free carbon dioxide..... = None
- (2) Calcium hardness..... = 35 ppm
- (3) Magnesium hardness..... = Desired amount
- (4) Total hardness..... = The sum of (2) and (3)
- (5) Alkalinity..... = 35 ppm + Number of ppm causticity in effluent

SECTION 57. (continued)

Check on Calculated Compositions of Effluent: The noncarbonate hardness should be reduced or the sodium alkalinity should be increased by the equivalent of the soda ash added (expressed as CaCO_3).

Alkalinity and pH of Effluent: The causticity will be the amount determined from section 53 and the remainder of the alkalinity will be carbonate alkalinity. The approximate pH may be determined from section 53.

Dosages of Chemicals Required: The dosages of commercial hydrated lime (93% Ca(OH)_2) or commercial chemical lime (90% CaO) and commercial soda ash (98% Na_2CO_3) required, in pounds per 1000 U. S. gallons, will be as follows:

	93% Hydrated Lime	or	90% Chemical Lime	98% Soda Ash
	-----Lbs. Per 1000 gal.-----			
Free carbon dioxide as ppm CO_2	X .0151		X .0118	None
Alkalinity as ppm CaCO_3	X .00663		X .00519	None
Magnesium hardness as ppm CaCO_3 to be removed.....	X .00663		X .00519	X .00901
Causticity in effluent as ppm CaCO_3	X .00663		X .00519	X .00901
Calcium noncarbonate hardness as ppm CaCO_3	None		None	X .00901

Class 2. Composition of Effluent: Treatment for reduction of calcium alkalinity to 35 ppm; reduction of magnesium alkalinity and removal of magnesium noncarbonate hardness will result in an effluent having the following composition:

- (1) Free carbon dioxide..... = None
- (2) Calcium hardness..... = 35 ppm
- (3) Magnesium hardness..... = Desired amount (see Section 53)
- (4) Total hardness..... = The sum of (2) and (3)
- (5) Alkalinity..... = 35 ppm

Check on Calculated Compositions of Effluent: The noncarbonate hardness should be reduced or the sodium alkalinity should be increased by the equivalent of the soda ash added (expressed as CaCO_3).

Alkalinity and pH of Effluent: The causticity of the effluent may be determined from section 72 and the remainder of the alkalinity will be carbonate alkalinity. The approximate pH may be determined from section 72.

Dosages of Chemicals Required: The dosages of commercial hydrated lime (93% Ca(OH)_2) or commercial chemical lime (90% CaO) and commercial soda ash (98% Na_2CO_3) required, in pounds per 1000 U. S. gallons, will be as follows:

	93% Hydrated Lime	or	90% Chemical Lime	98% Soda Ash
	-----Lbs. Per 1000 gal.-----			
Free carbon dioxide as ppm CO_2	X .0151		X .0118	None
Alkalinity as ppm CaCO_3	X .00663		X .00519	None
Magnesium alkalinity to be removed as ppm CaCO_3	X .00663		X .00519	None
Noncarbonate hardness to be removed as ppm CaCO_3	X .00663		X .00519	X .00901
Sodium alkalinity increase as ppm CaCO_3	X .00663		X .00519	X .00901

Class 3, Case I: Composition of Effluent: Treatment for reduction of calcium noncarbonate hardness will result in an effluent having the following composition:

- (1) Free carbon dioxide..... = None
- (2) Free mineral acid..... = None
- (3) Calcium hardness..... = Whatever amount is desired down to 35 ppm
- (4) Magnesium hardness..... = 90% of original magnesium hardness
- (5) Total hardness..... = The sum of (3) and (4)
- (6) Alkalinity..... = 35 ppm

Check on Calculated Compositions of Effluent: The noncarbonate hardness should be reduced or the sodium alkalinity should be increased by the equivalent of the soda ash added (expressed as CaCO_3).

Alkalinity and pH of Effluent: The 35 ppm of alkalinity will be carbonate alkalinity. The pH will be approximately 10.2.

SECTION 57. (continued)

Dosages of Chemicals Required: The dosages of commercial hydrated lime (93% $\text{Ca}(\text{OH})_2$) or commercial chemical lime (90% CaO) and commercial soda ash (98% Na_2CO_3) required, in pounds per 1000 U. S. gallons, will be as follows:

	93% Hydrated Lime	or	90% Chemical Lime	98% Soda Ash
	-----Lbs. Per 1000 gal.-----			
Free carbon dioxide as ppm CO_2	X .0151	X	.0118	None
Alkalinity as ppm CaCO_3	X .00663	X	.00519	None
Magnesium alkalinity to be removed as ppm CaCO_3	X .00663	X	.00519	None
Noncarbonate hardness to be removed as ppm CaCO_3	X .00663	X	.00519	X .00901
Sodium alkalinity increase as ppm CaCO_3	X .00663	X	.00519	X .00901

Class 3, Case 2: Composition of Effluent: Treatment for reduction of calcium hardness to 35 ppm and reduction of magnesium hardness to desired amount (see section 53) will result in an effluent of the following composition:

- (1) Free mineral acid..... = None
- (2) Free carbon dioxide..... = None
- (3) Calcium hardness..... = 35 ppm
- (4) Magnesium hardness..... = Desired amount (see Section 53)
- (5) Total hardness..... = The sum of (3) and (4)
- (6) Alkalinity..... = 35 ppm + number of ppm causticity in effluent

Check on Calculated Compositions of Effluent: The noncarbonate hardness should be reduced or the sodium alkalinity should be increased by the equivalent of the soda ash added (expressed as CaCO_3).

Alkalinity and pH of Effluent: The causticity of the effluent may be determined from section 61 and the remainder of the alkalinity will be carbonate alkalinity. The approximate pH may be determined from section 53.

Dosages of Chemicals Required: The dosages of commercial hydrated lime (93% $\text{Ca}(\text{OH})_2$) or commercial chemical lime (90% CaO) and commercial soda ash (98% Na_2CO_3) required, in pounds per 1000 U. S. gallons, will be as follows:

	93% Hydrated Lime	or	90% Chemical Lime	98% Soda Ash
	-----Lbs. Per 1000 gal.-----			
Free carbon dioxide as ppm CO_2	X .0151	X	.0118	None
Mineral acid as ppm CaCO_3	X .00663	X	.00519	X .00901
Magnesium hardness as ppm CaCO_3	X .00663	X	.00519	X .00901
Causticity in effluent as ppm CaCO_3	X .00663	X	.00519	X .00901
Calcium hardness as ppm CaCO_3	None		None	X .00901

SECTION 58. **RAILWAY LIME SODA TREATMENT** EXCESS CHEMICAL TREATMENT

Composition of Effluent: The so called "excess chemical lime soda process" is largely confined to railway practice where it is desired to secure, in the cold, an effluent low in hardness and with a considerable excess of both caustic and carbonate sodium alkalinity. The amounts of sodium alkalinity desired in the effluent vary in practice, but, in general, range between 5 and 9 grains per gallon (85 to 155 ppm). The amounts of magnesium and calcium in the effluent vary somewhat according to the amounts of caustic soda and sodium carbonate present. The following analysis shows the composition of a typical effluent:

- (1) Free carbon dioxide..... = None
- (2) Calcium hardness..... = 8 ppm
- (3) Magnesium hardness..... = 8 ppm
- (4) Total hardness..... = The sum of (2) and (3)
- (5) Alkalinity..... = 140 ppm

* The sodium alkalinity in this case is 124 ppm; causticity is 70 ppm; carbonate alkalinity is 70 ppm and the pH value is approximately 11.2.

SECTION 58. (continued)

Dosages of Chemicals Required: The dosages of commercial hydrated lime (93% Ca(OH)₂) or commercial chemical lime (90% CaO) and commercial soda ash (98% Na₂CO₃) required, in pounds per 1000 U. S. gallons, will be as follows:

	93% Hydrated Lime	or	90% Chemical Lime	98% Soda Ash
	-----Lbs. Per 1000 gal.-----			
Free carbon dioxide as ppm CO ₂	X .0151		X .0118	None
Alkalinity as ppm CaCO ₃	X .00663		X .00519	None
Magnesium hardness to be removed as ppm CaCO ₃	X .00663		X .00519	None
Causticity desired in effluent as ppm CaCO ₃	X .00663		X .00519	None
Total noncarbonate hardness as ppm CaCO ₃	None		None	X .00901
* Sodium alkalinity desired in effluent as ppm CaCO ₃	None		None	X .00901

* With water containing sodium alkalinity, the dosage of soda ash employed can be decreased by the number of ppm of sodium alkalinity in the modified analysis.

Section 59. **REDUCTION OF ALKALINITY IN WATERS CONTAINING SODIUM ALKALINITY
BY THE COLD LIME, CALCIUM CHLORIDE (OR SULFATE) PROCESS**

The Lime Calcium Chloride Process: The reduction of alkalinity in waters containing sodium urn alkalinity (or less than 80 ppm noncarbonate hardness expressed as CaCO₃) may be accomplished by treatment with hydrated lime and calcium chloride (or calcium sulfate). This process is especially applicable to the beverage industry where an effluent of low alkalinity-usually about 50 ppm-is required and where noncarbonate hardness is of little or no importance. The alkalinity reduction in this process is effected as follows:

Sodium alkalinity may be reduced to zero by treatment with hydrated lime and calcium chloride.

Calcium alkalinity may be reduced to 35 ppm by treatment with hydrated lime.

Magnesium alkalinity: If less than 80 ppm, 10% may be removed by hydrated lime and the remainder may be reduced to any desired figure by treatment with calcium chloride. If more than 80 ppm, it may be reduced to 80 ppm by treatment with hydrated lime, and the 80 ppm remaining may be reduced to any desired figure by treatment with calcium chloride.

Composition of Effluent: The composition of the effluent will be as follows:

- (1) Free carbon dioxide = None
- (2) Sodium alkalinity..... = None
- (3) Calcium alkalinity..... = 35 ppm
- (4) Magnesium alkalinity..... = Desired amount (see Section 51)
- (5) Alkalinity..... = The sum of (3) and (4)
- (6) Calcium hardness..... (3)
- (7) Magnesium hardness..... = 90% of original magnesium hardness if 80 ppm or less is present
or Magnesium hardness..... = 80 ppm if more than 80 ppm original magnesium hardness is present
- (8) Total hardness..... = The sum of (3) and (7)

Check on Calculated Compositions of Effluent: The noncarbonate hardness should be increased or the sodium alkalinity should be reduced by the equivalent of the calcium chloride or sulfate added (expressed as CaCO₃).

Alkalinity and pH of Effluent: All of the alkalinity in the effluent will be carbonate alkalinity. The approximate pH may be determined from section 53.

SECTION 59. (continued)

Dosages of Chemicals Required: The dosages of commercial hydrated lime (93% $\text{Ca}(\text{OH})_2$) or commercial chemical lime (90% CaO) and commercial calcium chloride (75% CaCl_2) or commercial powdered gypsum (79% CaSO_4) required, in pounds per 1000 U. S. gallons, will be as follows:

	93% Hydrated Lime	or	90% Chemical Lime	75% Calcium Chloride	or	79% Calcium Sulfate
	-----lb. Per 1000 gal.-----					
Free carbon dioxide as ppm CO_2	X .0151		X .0118	None		None
Alkalinity as ppm CaCO_3	X .00663		X .00519	None		None
* Magnesium hardness to be removed as ppm CaCO_3	X .00663		X .00519	None		None
Sodium alkalinity as ppm as CaCO_3	None		None	X .0123		X .0143
** Magnesium alkalinity as ppm CaCO_3 requiring CaCl_2 or CaSO_4	None		None	X .0123		X .0143

* If original magnesium hardness is 80 ppm or less, use 10% of original magnesium hardness

If original magnesium hardness is above 80 ppm, use number of ppm original magnesium hardness - 80 ppm

** If original magnesium hardness is less than 80 ppm, use 90% of the number of ppm original magnesium hardness-(ppm magnesium alkalinity desired in effluent + original noncarbonate hardness).

If original magnesium hardness is over 80 ppm, use 80 ppm -(ppm magnesium alkalinity desired in effluent + original noncarbonate hardness).

Note: Calcium chloride, in flake or solid form, varies in moisture content from 27% to 20%. The figure of 75%, used in the calculation, refers to calcium chloride having moisture content of 25% and this is close enough for preliminary calculations. Powdered gypsum contains 21% of combined water so the figure of 79% CaSO_4 , used in the calculations, is close enough for all practical purposes.

Note: 1.0 lb. 75%, calcium chloride per 1000 gal. increases the chloride content, expressed as Cl, by 57.6 ppm

1.0 lb. powdered gypsum (79% CaSO_4) per 1000 gal. increases the sulfate content, expressed as SO_4 , by 55.7 ppm

